1999

Methyl Methacrylate from Methyl Acetylene via Carboxymethylation

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The worldwide demand for the use of MMA in plastics, resins, extrusions compounds, chemical intermediates, etc. is well documented. To satisfy this demand, we have successfully designed a plant to produce 111 MM lbs./yr. of 99.9% pure MMA at full capacity. The subsequent economic analysis of this design showed a return on investment after the third year of production of 56.3% and an investor's rate of return of 39.5%. Based on these returns, and on the environmental and safety advantages of this production method over others currently in use, we highly recommend the construction of this plant beginning in April 2000.

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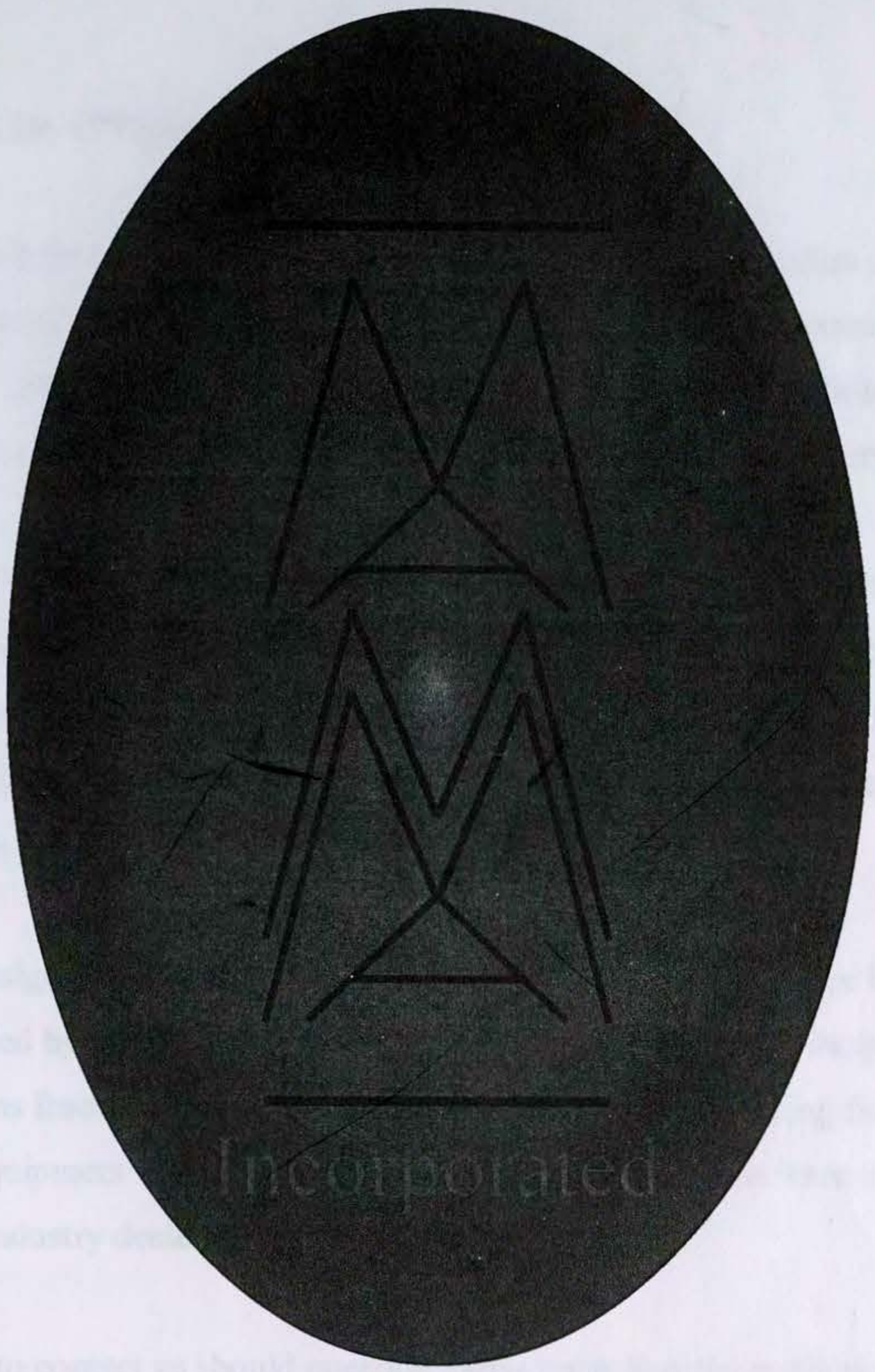

Chris Brinkerhoff, Adam McCabe, Nitin Natesan

Spring 1999

Dr. Arnold Kivnick

Dr. Patrick O'Flynn

Department of Chemical Engineering

Philadelphia, PA 19104

Dr. Kivnick and Dr. O'Flynn:

Enclosed you will find our recommended plant design for the production of methyl methacrylate via the carboxymethylation reaction outlined in Shell patented technologies US 3,671,605, 5,081,286, and 5,719,313. The plant is located on the United States Gulf Coast and has the capacity to produce 100 MM pounds of methyl methacrylate per year.

Economic, control feasibility, and market price sensitivity analyses were conducted for the process, which was simulated in steady-state using ASPEN® v. 10.0 software. Environmental and plant safety comparisons were also made with the methyl methacrylate via dehydration of methyl 2-hydroxyisobutyrate process that has been recommended in years prior.

Overall plant designs, unit designs, and economic analysis methods were based on heuristics outlined by Seider, Seader, and Lewin's *Process Design Principles* as well as recommendations from various consultants in the chemical engineering field. Costs for materials and equipment unique to the carboxymethylation process were obtained, when possible, from industry dealers.

Please feel free to contact us should questions arise regarding the methodology used in completing this report.

Sincerely,

Christopher Brinkerhoff | Adam McCabe | Nitin Natesan

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I. ABSTRACT

Previous process designs and current world demand for methyl methacrylate (MMA) have necessitated the investigation of the feasibility of designing a new MMA production process. The most commonly used industrial process for MMA production is the acetone cyanohydrin (ACH) process, which has the disadvantage of using large quantities of hydrogen cyanide (HCN). HCN is both an environmental and a health hazard if not handled properly. The Shell Oil Company has developed a process where the use of HCN can be avoided. In this process, methyl acetylene (MA) is converted to MMA by reaction with high-pressure carbon monoxide gas and methanol over a palladium catalyst. We have therefore considered the construction of a plant capable of producing 100 MM lbs./yr. of MMA at a United States Gulf Coast location via the carboxymethylation of methyl acetylene.

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II. INTRODUCTION

Description of the Product

Methyl methacrylate is a clear, colorless, flammable liquid organic compound. Its molecular formula is $C_5H_8O_2$. MMA can be polymerized to poly (methyl methacrylate), or PMMA, which is more commonly known as Plexiglas® or Lucite®. MMA also serves as an intermediate to other acrylics and more complex methacrylates. Acrylics such as MMA are known for their outstanding transparency, resistance to outdoor exposure, and high surface gloss. MMA is also relatively light in weight making it suitable for use as a substitute for glass, as described by the University of Southern Mississippi's *Macrogalleria* internet site (http://www.psrc.usm.edu/macrog/pmma.html):

> "When it comes to making windows, PMMA has another advantage over glass. PMMA is more transparent than glass. When glass windows are made too thick, they become difficult to see through. But PMMA windows can be made as much as 13 inches (33 cm) thick, and they're still perfectly transparent. This makes PMMA a wonderful material for making large aquariums, whose windows must be thick in order to contain the high pressure millions of gallons of water. In fact, the largest single window in the world, an observation window at California's Monterrey Bay Aquarium, is made of one big piece of PMMA which is 54 feet long, 18 feet high, and 13 inches thick (16.6 m long, 5.5 m high, and 33 cm thick)."

MMA is available in liquid form as a monomer and in solid form as polymeric sheets or pellets of various thicknesses. Different methods of processing MMA into a polymer lead to distinct grades that suit various applications. Examples of these applications include the use of MMA as a "cement" in total joint replacement technology as well as in several other types of medical reconstructive procedures.

Market Opportunity

The market for MMA has been steadily growing throughout the past decade, as it has remained a commonly traded chemical commodity. Worldwide MMA production centers provide a steady supply of MMA to the ever increasing demands of international consumers, as explained on the Chemical Industries Newsletter internet site (http://www-cmrc.sri.com/CIN/1997/January-February/Article03.html):

> "Methyl methacrylate monomer (MMA) is by far the most important methacrylic acid ester available commercially. The world MMA consumption in 1996 amounted to 2.8 billion pounds of MMA valued at over $2.1 billion…The global capacity utilization rate was approximately 84% in 1995, decreasing slightly in 1996 to 83%. Capacity utilization in Asia was very low, due primarily to shortages of acetone cyanohydrin feedstock in the People's Republic of China. MMA and, to a lesser degree, methacrylic acid (MAA) are largely captive markets. Most producers consume large amounts, either domestically or in foreign plants or subsidiaries, in their acrylic resin, acrylic sheet, or surface coating operations."

This section describes why we believe entering the MMA market at this time appears to be very attractive.

Description of the Process

The process investigated in this report is based on a new chemical reaction developed by Shell Corporation. The Shell process involves the carboxymethylation of methyl acetylene (MA) with a three-part catalyst to produce methyl methacrylate. The catalyst consists of methanesulfonic acid, bis(3-chlorophenyl)(2-pyridyl)phosphine and palladium (II) acetate. This process is considered especially attractive because it produces MMA at high yields in one step. The largest concerns with this new process are

the hazards associated with handling methanesulfonic acid (MSA) and the high purity of methyl acetylene required for the catalyst to be active.

These two concerns were resolved in this design. The handling of MSA required the use of specially lined corrosion resistant equipment. The MSA in this process is recycled through a small segment of the plant, which reduces the amount of acid handled, which reduces the amount of corrosion resistant equipment necessary. The MA was found in the waste stream of an ethylene plant. This stream is roughly one quarter MA and one quarter propadiene (PD) an isomer of MA. The other half of the stream is propane, which raises the autoignition temperature to a safe level during operation. The methyl acetylene in this stream must be purified in an isomerization reactor and an extractive distillation column before it can be fed to the carboxymethylation reactor.

The specified production rate of 100 MM lbs./yr. of MMA is limited by the capacity of the naphtha cracking plant, which supplies the C_3 feed stream. Creation of a larger plant would require feed streams from multiple naphtha cracking plants. The plant would be located in the U.S. Gulf Coast, next to a naphtha cracking plant to minimize transportation costs of the hydrocarbon feed stream. The Gulf Coast is a common location for chemical plants because of availability of labor, efficiency of the workforce and the beneficial local rules and customs.

The environmental and safety considerations of handling all the chemicals within this process were evaluated. The use of MSA in the process necessitates the use of equipment that is lined with corrosion resistant materials. MSA is a hazardous chemical that requires careful storage. The MSA is transferred to the catalyst manufacturer to recover the palladium dissolved in the catalyst solution. Carbon monoxide is also a

reactant that requires careful handling, but it is not stored within the plant. The methyl crotonate byproduct is produced in very low amounts and can be incinerated.

Alternative Production Methods

Currently the most common process for producing methyl methacrylate is the acetone cyanohydrin (ACH) process. This process converts acetone and hydrogen cyanide (HCN) to MMA in three steps. In the ACH process, large proportions of sulfuric acid are used, and disposal of the acidic byproduct is expensive. The Mitsubishi Gas Chemical Company, Inc. developed an alternative method of converting acetone and HCN to MMA that requires four steps. The disadvantages of process include the involvement of many catalysts, the production of a larger number of byproducts, and a more complex purification procedure. However, this process drastically reduces the amount of HCN handled.

Alternative processes with other raw materials are under development, and several plants based on a new four carbon (C_4) process have been built in Japan. The C_4 process is based on two-tray vapor-phase oxidation of isobutylene or *tert*-butanol. Two other possible chemical reactions are the direct oxidation process, which combines 1,1-dimethyl ethylene with oxygen and methanol, and the direct methacrylate process, which oxidizes and esterifies methacrolein to produce MMA.

Project Goals

The goal of this project is to design a plant capable of producing 100 MM lb./yr. of methyl methacrylate using the new Shell process. The proposed design is controllable and environmentally friendly. Raw material, energy consumption, and waste disposal are minimized to a financially justified extent.

T110
C3 HOLDUP TANK

P110
C3 FEED PUMP

R150
ISOMERIZATION REACTOR

T210
METHANOL HOLDUP TANK

P210
METHANOL FEED PUMP

P230
METHANOL EXTRACTION FEED PUMP

D250 & 251
EXTRACTIVE DISTILLATION COLUMNS

P255
REFLUX PUMP

T255
REFLUX ACCUMULATOR

C260
CONDENSER

K270
REBOILER

P270
BOTTOMS PUMP

P280
DISTILLATE PUMP

T295
PROPANE HOLDUP TANK

T310
PdAC2 HOLDUP TANK

T320
BCPPP HOLDUP TANK

T330
MSA HOLDUP TANK

A350
CATALYST AGITATOR

M350
CATALYST MIXING TANK

P350
CATALYST BATCH FEED PUMP

P390
CATALYST REACTOR FEED PUMP

T395
CATALYST WASTE HOLDUP TANK

H410
PRE-REACTION HEAT EXCHANGER

H460
REACTOR HEAT EXCHANGER

R450
CSTR

A450
REACTOR AGITIATOR

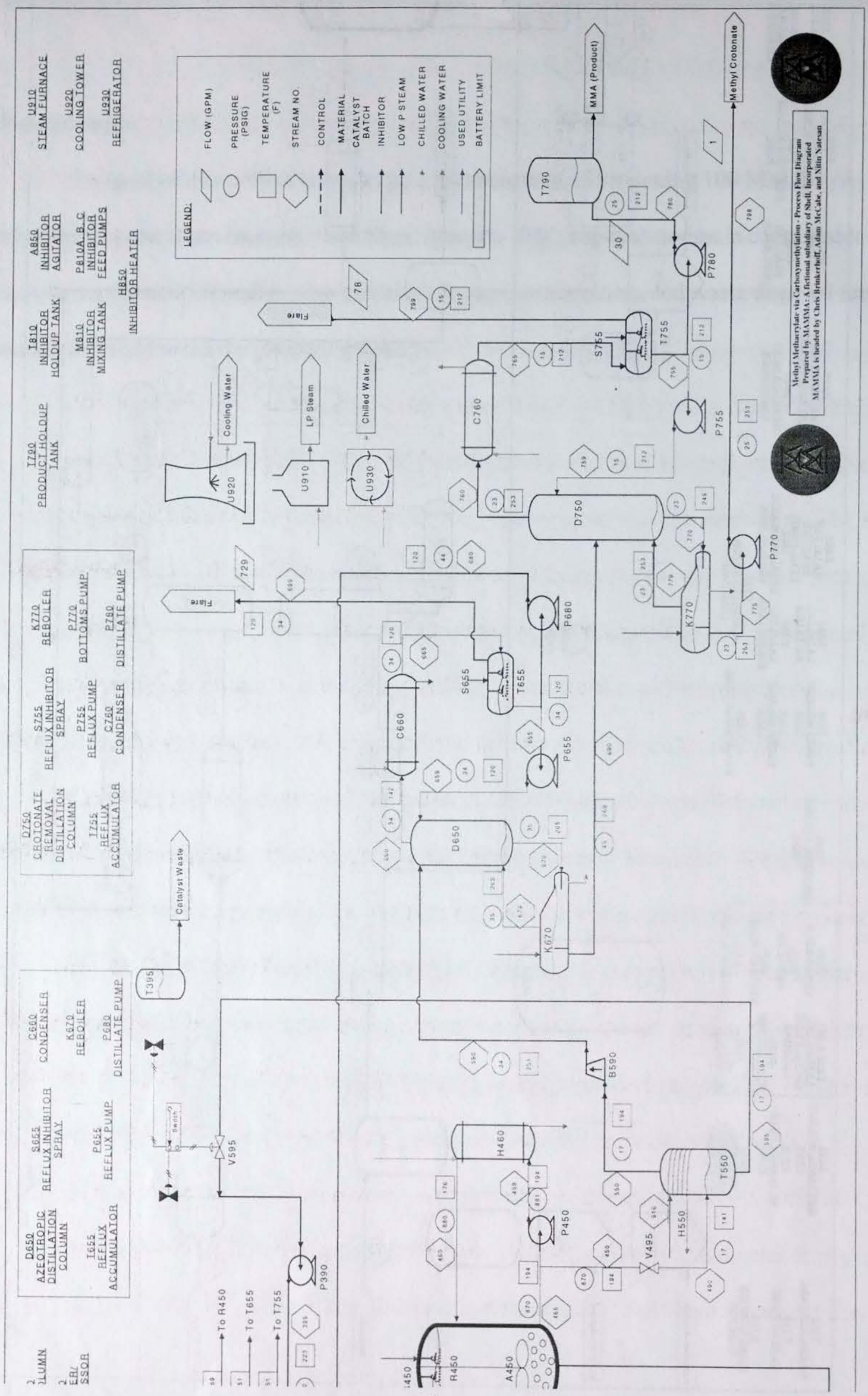
S450
REACTOR INHIBITOR SPRAY

P450
REACTOR REFLUX PUMP

T550
FLASH COL

B590
BLOWER COMPRES

Palladium Acetate
BCPP Phosphine
MSA
Methanol
C-3 Feed
Carbon Monoxide
4-methoxyphenol
Impure Propane
Flare
S4


LEGEND:
FLOW (GPM)
PRESSURE (PSIG)
TEMPERATURE (F)
STREAM NO.
CONTROL
MATERIAL
CATALYST BATCH
INHIBITOR
LOW P STEAM
CHILLED WATER
COOLING WATER
USED UTILITY
BATTERY LIMIT
U910 STEAM FURNACE
U920 COOLING TOWER
U930 REFRIGERATOR
A850 INHIBITOR AGITATOR
P810A,B,C INHIBITOR FEED PUMPS
H850 INHIBITOR HEATER
I810 INHIBITOR HOLDUP TANK
M810 INHIBITOR MIXING TANK
I790 PRODUCT HOLDUP TANK
S755 REFLUX INHIBITOR SPRAY
K770 REBOILER
P770 BOTTOMS PUMP
P755 REFLUX PUMP
P780 DISTILLATE PUMP
C760 CONDENSER
D750 CROTONATE REMOVAL DISTILLATION COLUMN
I755 REFLUX ACCUMULATOR
D650 AZEOTROPIC DISTILLATION COLUMN
I655 REFLUX ACCUMULATOR
S655 REFLUX INHIBITOR SPRAY
P655 REFLUX PUMP
C660 CONDENSER
K670 REBOILER
P680 DISTILLATE PUMP
Cooling Water
LP Steam
Chilled Water
Flare
Catalyst Waste
To R450
To T655
To T755
MMA (Product)
Methyl Crotonate
Methyl Methacrylate via Carboxymethylation - Process Flow Diagram
Prepared by MAMMA: A fictional subsidiary of Shell, Incorporated
MAMMA is headed by Chris Brinkerhoff, Adam McCabe, and Nitin Vatsan

IV. PROCESS DESCRIPTION

The primary feed stream enters the plant from a neighboring naphtha cracking plant and is composed of a mix of C_3 hydrocarbons. Stream (110), which consists of 48.5% propane, 25% methyl acetylene, 25% propadiene, and 1.5% propylene enters the process as a liquefied gas from a 1 day storage tank (T-110) at 175 psi and ambient temperature. The C_3 feed pump (P-110) increases the pressure of the stream to 326 psi and feeds the isomerization reactor (R-150). The isomerization reaction occurs over a potassium carbonate catalyst and is maintained between 77 and 87 °F to ensure 80% of the propadiene is converted to methyl acetylene. The outlet of the isomerization chamber, stream (190), is then fed to the extractive distillation column (D-250). The process block diagrams in Appendix J outline each section of the plant.

The main function of the extractive distillation column is to separate propadiene from methyl acetylene. The propadiene is removed because the palladium catalyst in the main reaction becomes less effective if the composition of propadiene in the reaction feed exceeds 1.9%. Methanol is used as a mass separating agent to assist the separation of the two components. Methanol was chosen as the mass separating agent because it is also a reactant later in the process. The column has 150 trays and operates at 250 psi. The distillate of the extractive distillation column is predominantly composed of propane and is sent to the C_3 byproduct storage tank (T-295) via stream (280). The contents are then sold to the naphtha cracking plant at fuel value. The bottoms product of the extractive distillation column, stream (275), undergoes an increase in pressure to 870 psi through the extraction bottoms pump (P-270). Stream (290) is cooled to 176 °F in the reactor feed heat exchanger (H-410) and sent to the carboxymethylation reactor (R-450).

Stream (410) travels from the reactor feed heat exchanger to the reactor (R-450), where it mixes with the carbon monoxide and catalyst feeds from streams (340) and (395), respectively, and the reaction takes place. The reaction is highly exothermic and requires cooling. An external heat exchanger (H-460) mounted beside the reactor takes a fraction of the effluent at 194 °F, cools it to 176 °F, and recycles the stream back into the top of the reactor. This reflux absorbs the heat generated by the reaction. A schematic diagram of the reactor is shown in the Section VI. The reactor converts greater than 99.9% of the methyl acetylene to products. The reaction is 98.5% selective for methyl methacrylate, while the remainder is methyl crotonate byproduct. The catalyst used is palladium (II) acetate and bis(3-chlorophenyl)(2-pyridyl)phosphine dissolved in methanesulfonic acid. The reactor and the heat exchanger are lined with Hastelloy-C to protect them from being corroded by the MSA.

The chemical reaction presented by Shell in U.S. patent 5,719,313 describes a homogeneous mixture with the catalyst in solution. If a solid catalyst system which achieves the same reaction under the same conditions could be designed, a packed bed reactor would be used, and the only unit that would need to be Hastelloy-C lined would be the reactor. Research into the feasibility of this type of supported catalyst is recommended as a method for reducing the capital cost of the plant. We designed our process by evaluating the data outlined in the Shell experiments, but it is worthwhile to investigate this alternative chemical process.

After the reactor, stream (450) is passed through a pressure reduction valve (V-495) to change the pressure from 870 psi to 16.8 psi. A turbine was considered to recover some of the energy that is lost in the pressure reduction, but it was not implemented in

our design. A turbine operating at 100% efficiency would be able to recover 174 hp (130 kW), which translates to a savings $41 M per year in electricity costs. However, the amount saved is minute in comparison to the total utilities cost of $2 MM per year. Industrial consultants advised us not to use a turbine because turbines frequently break down, which compromises the reliability of the entire plant.

After stream (450) passes through the valve, it is flashed in the catalyst flash column (T-550) at a pressure of 16.8 psi. To reduce the total plant cost, the number of units lined with Hastelloy-C is reduced by removing the acid in the first separation step. The liquid stream (595) from the bottom of the flash column, which contains the catalyst along with some of the reaction products, is recycled back to the reactor. The palladium catalyst is very expensive and discarding it after one use is not economical. The pressure of the flash vessel was set to ensure that the vapor stream (550) has less than 1 PPM of methanesulfonic acid. The blower (B-590), increases the pressure of stream (550) and sends it to the azeotropic distillation column (D-650).

A flash column was used to remove the catalyst from the reaction products because a single flash is the least expensive method for this separation. Two other systems for this separation were evaluated: replacing the flash vessel with a distillation column and adding a second flash vessel. Each method was designed to purify the reactor effluent to contain less than 1 PPM of MSA. The distillation column considered above was designed without a condenser, because the use of a condenser increased the temperature and heat duty of the reboiler, making the column more expensive than necessary. The cost of utilities and size of the column was minimized to find the optimal column configuration (see Figure 1, p. 12). This column is able to produce a distillate stream with

only 1 PPM acid and a bottoms stream that is predominately catalyst (>90 mol%). This separation sequence greatly reduces the amount of material in the catalyst recycle stream (395) compared to the alternatives considered. The reboiler temperature was 387 °F, which requires high pressure steam. The additional cost of high pressure steam increases the utilities cost of the column and makes it a less attractive option than one flash. If a situation could be developed to reduce the temperature in the reboiler and heat it with low pressure steam, this would be the least expensive separation method (see Figure 2, p. 13 and Appendix I).

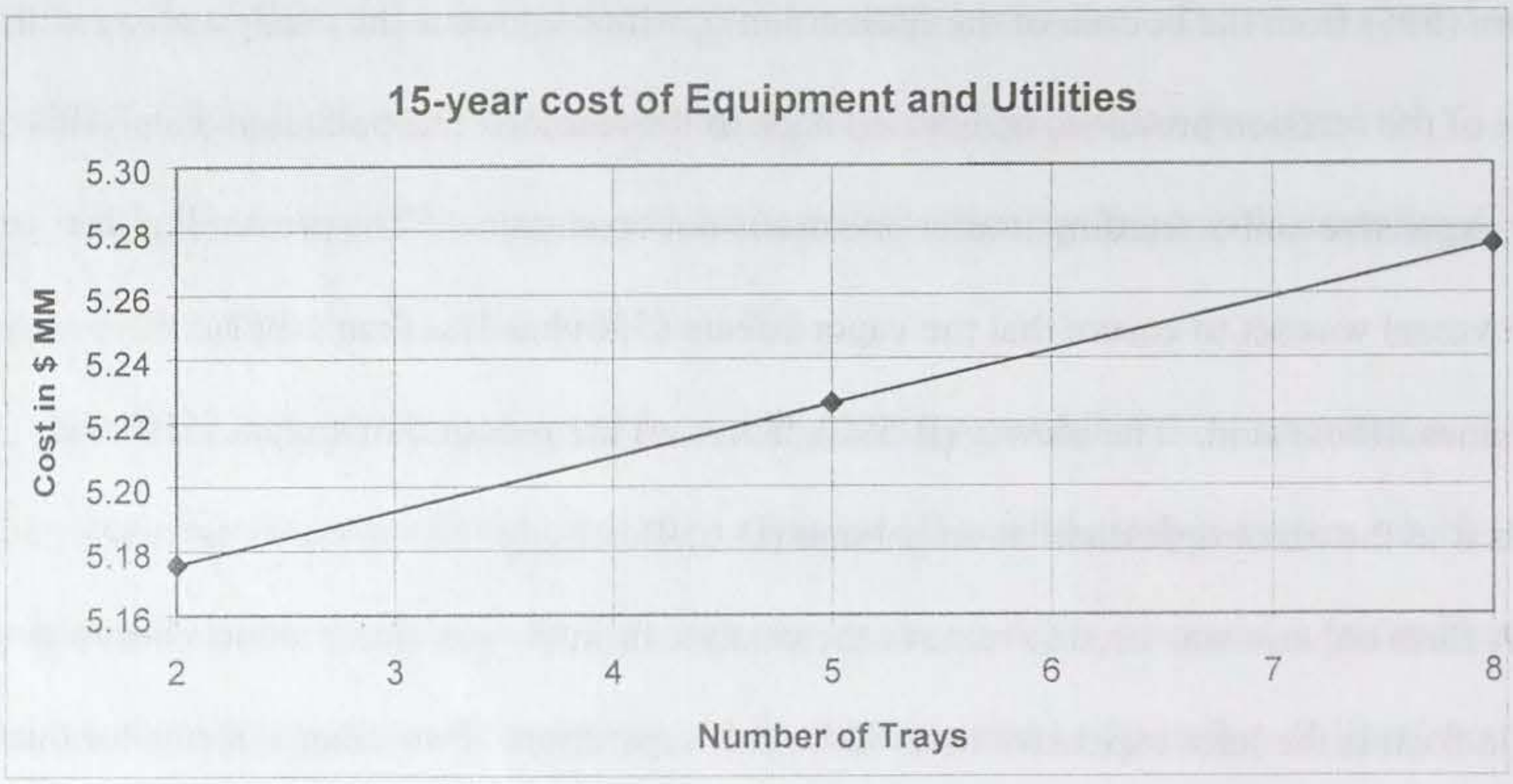


Figure 1: Effect of the number of trays in the catalyst removal distillation column on the cost of the rest of the process.

A two flash separation sequence was considered because, in practice, it is a simplification of the sequence involving a column. Two flash vessels are the same as the two trays on a column without the reboiler or the condenser. The second flash vessel decreases the amount of material in stream (395). The savings from the reduced size of the reactor and the catalyst reactor feed pump (P-390) was not sufficient to offset the cost of the second flash vessel (see Figure 2, p. 13 and Appendix I).

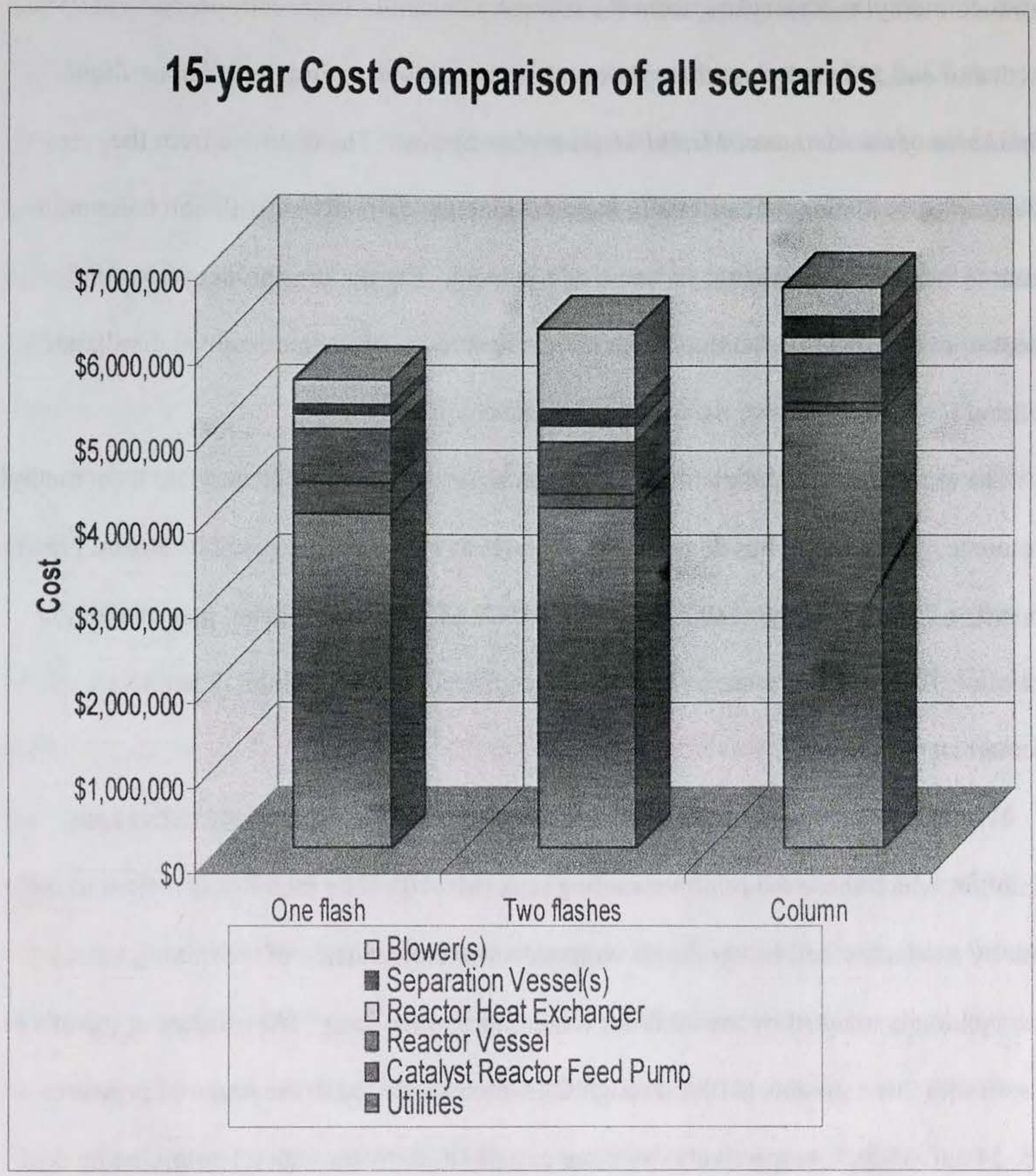


Figure 2: Cost comparison of three separation scenarios for catalyst removal. The cost represented in this graph is the combined cost of all equipment and utilities affected by catalyst removal. "Column" is a 2 tray distillation column without a condenser.

The azeotropic distillation column has 11 trays and operates at 34 psi to separate the product, methyl methacrylate, from the solvent, methanol. An azeotrope exists at 95% methanol and 5% methyl methacrylate at these conditions according to *Vapor-Liquid Equilibria of the Methanol-Methyl Methacrylate System*. The distillate from the azeotropic distillation, stream (680), is recycled to the extractive distillation column in order to recover the methanol for reuse as a solvent. The bottoms product from the azeotropic distillation column (stream 690) is sent to the crotonate removal distillation column (D-750) to remove the methyl crotonate byproduct.

The crotonate removal distillation column separates methyl methacrylate from methyl crotonate. The column has 88 trays and operates at 14.7 psi. The distillate stream (755) consists of 99.9% methyl methacrylate with 10 PPM 4-methoxyphenol polymerization inhibitor. The bottoms stream (775) contains methyl crotonate which is sent to an incinerator for disposal.

The inhibitor holdup tank (T-810) contains 4-methoxyphenol, a polymerization inhibitor, which feeds the inhibitor mixing tank (M-810). The inhibitor is melted in the tank by an electric coil heater that is wrapped around the outside of the mixing vessel. The melting is assisted by the inhibitor mixer agitator (A-850). The effluent of the mixer is split into three streams (810A through C), which are raised to the required pressures (25, 34 and 880 psi, respectively) by three pumps (P-810A through C) before being sent to the carboxymethylation reactor (R-450), the azeotropic distillation reflux accumulator (T-655), and the crotonate removal reflux accumulator (T-755) via streams (815A through C). The cooling tower, steam furnace, and refrigerator (U-910 through 930) provide the necessary utilities to the rest of the plant.

V. ENERGY BALANCE

The Utility Cost Summary (p. 17) describes the energy demand of each unit, the method of satisfaction for each demand, and the cost of utilities required to fulfill the demand the each unit requires. The most expensive utility is steam, which is used in the reboilers (K-270, K-670, K-770) and the flash vessel (T-550). These units comprise 92% of the total utility cost (see Figures 3 and 4, p. 18). Heat integration for these units was evaluated, but a hot stream at the required temperature to heat the contents of the reboiler is not available in this process. The additional difficulty, from a control viewpoint, in integrating reboilers makes heat integration an unattractive undertaking, even if a suitable stream existed in the process.

Integration of cooling water was also considered. Cooling water is used in the condenser for each column (C-260, C-660, C-760) and both heat exchangers (H-410, H-460). Interconnection of cooling water streams in condensers and heat exchangers would also make controlling the plant much more difficult. A disturbance in one area would affect the flow rate of cooling water to that unit. By adjusting the flow rate of cooling water to that unit the flow rate to the next unit would be affected and could cause that unit to become unstable. The benefit of having a more reliable operation of the plant greatly overweighs the relatively small economic benefit of integrating cooling water streams.

The isomerization reactor (R-150) uses a chilled water stream (930). Chilled water exits the isomerization reactor via stream (930) at 67 ^{o}F. Heat integration of this stream was not pursued because the flow rate of stream (930) is small compared to the required flow rate of cooling water in the other heat exchangers. The additional

complexity of plant design and control, as described above, makes integration of this stream undesirable.

Recovery of energy from the high pressure stream leaving the carboxymethylation reactor (R-450) was investigated. The unit directly following the reactor is the catalyst removal flash vessel (T-550) which operates at 16.8 psi. Using a turbine to recover power from stream (450) could only offer 174 hp (130 kW), assuming a 100% efficiency. This would result in a savings of $41 M, which is a sufficiently small fraction of the total utilities costs to justify its omission from the design. Industrial consultants and the heuristics outlined in Appendix X of *Process Design Principles* both discourage the use of a turbine for this amount of power recovery, because turbines break down frequently and reduce the reliability of the plant.

V. UTILITY COST SUMMARY

ID	Name	Utility	Utility Source	Amount lb MMA	Cost Unit ($)	Cost year ($)	% of total
A-350	Catalyst Mixer Agitator	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
A-450	Reactor Agitator	Elec. (kWhr)	power company	3.70E-04	0.04	1,480	0.1%
A-810	Inhibitor Mixer Agitator	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
B-590	Flash Blower	Elec. (kWhr)	power company	9.82E-03	0.04	39,300	2.0%
C-260	Extract Condenser	C.W. (gal)	stream 921	3.75	0.00005	18,700	0.9%
C-660	Azeotropic Condenser	C.W. (gal)	stream 924	5.66	0.00005	28,300	1.4%
C-760	Remove Crotonate Condenser	C.W. (gal)	stream 925	4.99	0.00005	25,000	1.3%
H-410	Pre-Reaction Heat. Ex.	C.W. (gal)	stream 922	0.79	0.00005	3,950	0.2%
H-460	Reactor Heat Ex.	C.W. (gal)	stream 923	3.98	0.00005	19,900	1.0%
K-270	Extract Reboiler	Steam (lb)	stream 910	0.98	0.006	585,200	29.6%
K-670	Azeotropic Reboiler	Steam (lb)	stream 912	0.69	0.006	413,500	20.9%
K-770	Remove Crotonate Reboiler	Steam (lb)	stream 914	0.94	0.006	562,900	28.5%
P-110	C_3 Feed Pump	Elec. (kWhr)	power company	5.65E-04	0.04	2,260	0.1%
P-210	Methanol Feed Pump	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
P-230	Methanol Extract Pump	Elec. (kWhr)	power company	6.34E-04	0.04	2,540	0.1%
P-255	Extract Reflux Pump	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
P-270	Extract Bottoms Pump	Elec. (kWhr)	power company	2.57E-03	0.04	10,270	0.5%
P-280	Extract Dist. Pump	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
P-390	Catalyst Feed Pump	Elec. (kWhr)	power company	1.60E-04	0.04	640	<0.1%
P-450	Reactor Pump	Elec. (kWhr)	power company	8.47E-04	0.04	3,400	0.2%
P-655	Azeotropic Reflux Pump	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
P-680	Azeotropic Dist. Pump	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
P-755	Crotonate Reflux Pump	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
P-770	Crotonate Bottom Pump	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
P-780	Crotonate Distillate Pump	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
P-811	Inhibitor – Reactor Pump	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
P-813	Inhibitor – Azeotropic Pump	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
P-814	Inhibitor – Crotonate Pump	Elec. (kWhr)	power company	5.90E-05	0.04	236	<0.1%
R-150	Isomerization Reactor	C.W. (gal)	stream 930	5.92E-02	0.00005	296	<0.1%
T-550	Catalyst Flash Column	Steam (lb)	stream 916	4.27E-01	0.006	256,000	13.0%
U-930	Refrigeration	Refrig. (ton-days)	Refrigeration unit	3.77E-08	1.95	7,350	0.4%
					Total	**1,977,000**	**100%**

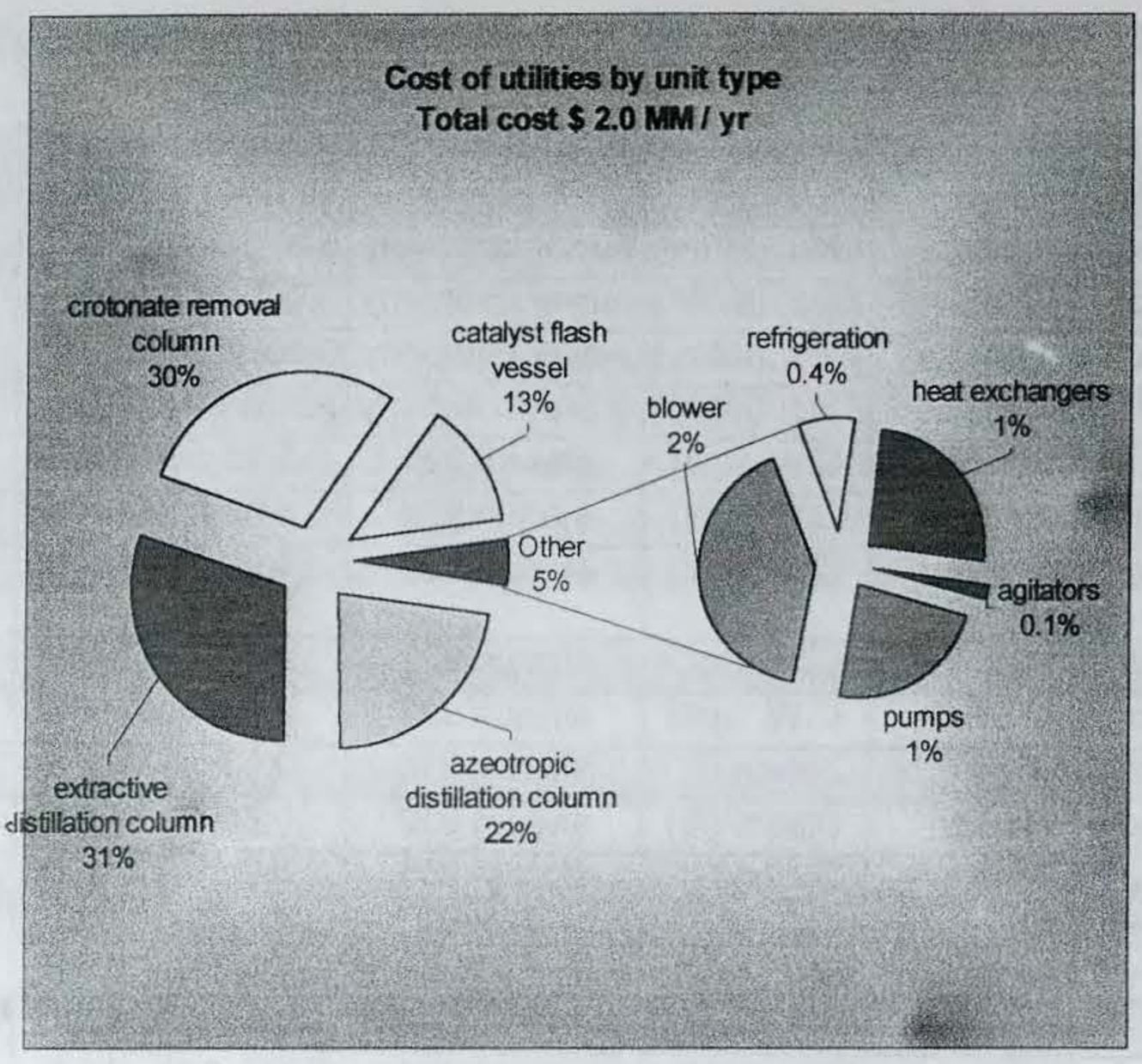


Figure 3: A breakdown of the cost of utilities used by the plant, sorted by unit.

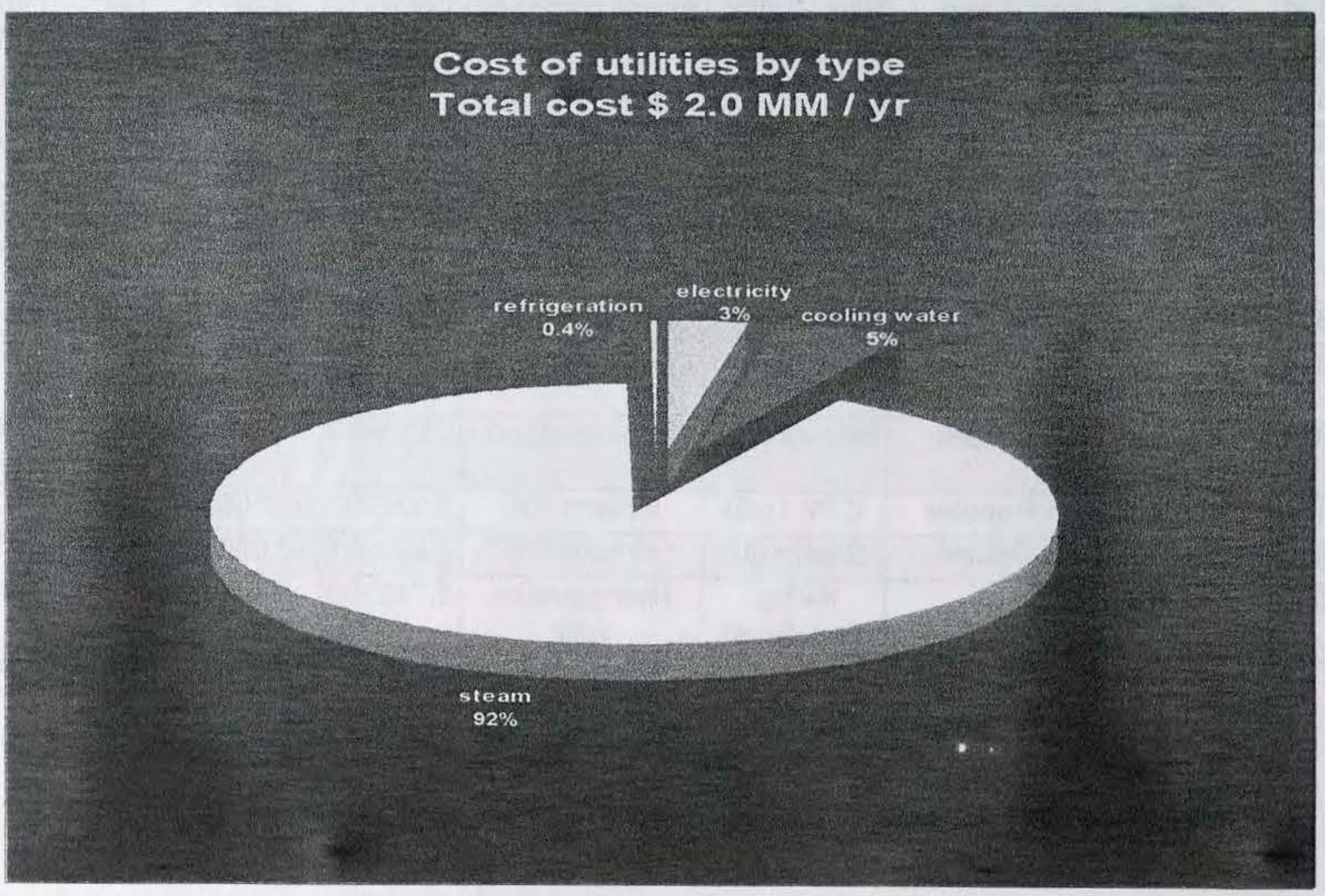


Figure 4: A breakdown of the cost of utilities used by the plant, sorted by utility type.

VI. UNIT DESCRIPTIONS

Catalyst Mixer Agitator (A-350)

The catalyst mixer agitator (A-350) facilitates the dissolution of palladium (II) acetate and bis(3-chlorophenyl)(2-pyridyl)phosphine in methanesulfonic acid in the catalyst mixer (M-350). An impeller achieves the agitation in the 10" diameter tank. The tip speed of the impeller is 10 ft/min and the superficial velocity is 0.5 ft/sec. The impeller blades are 1" wide and are located 3.5" from the bottom of the tank. The agitator was sized based on heuristics outlined in Appendix X of *Process Design Principles*. The agitator is constructed of Hastelloy-C because the concentration of methanesulfonic acid is high enough to corrode carbon steel. The mixer functions as a batch operation, and a new batch of catalyst must be made every month.

The agitator requires 745 W of electricity for operation, but we assumed that a 745 W motor would be among the smallest available motors for this type of operation. Our estimation of the bare module cost of the agitator for similar industrial applications is $1,500.

The specifications for this unit are summarized in the specification sheet on page 63, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit is included in Appendix F.

Reactor Agitator (A-450)

The Reactor Agitator (A-450) facilitates the reaction of methyl acetylene with carbon monoxide, methanol, and the three-part catalyst in the carboxymethylation reactor (R-450). An impeller achieves continuous agitation in the 7' 6" diameter tank. The tip

speed is 10 ft/min and the superficial velocity is 1.0 ft/sec. The blades are 6" wide and are located 2' 6" off the bottom of the tank. The agitator was sized based on heuristics outlined in Appendix X of *Process Design Principles*. The agitator is constructed of Hastelloy-C because of the highly corrosive nature of methanesulfonic acid. The agitator requires 4.67 kW of electricity for operation. Our estimation of the bare module cost of the agitator for similar industrial applications is $1,500.

The specifications for this unit are summarized in the specification sheet on page 64, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Inhibitor Mixer Agitator (A-850)

The inhibitor mixer agitator (A-850) facilitates the melting of 4-methoxyphenol in the inhibitor mixer (M-810). An impeller achieves continuous agitation in the 16" diameter tank. The tip speed of the impeller is 10 ft/min and the superficial velocity is 0.5 ft/sec. The impeller blades are 1" wide and are located 6" from the bottom of the tank. The agitator was sized based on heuristics outlined in Appendix X of *Process Design Principles*. The agitator is constructed of carbon steel because only the non-corrosive chemicals are used in the inhibitor mixer.

The agitator requires less than 745 W of electricity for operation, but we assumed that a 745 W motor would be among the smallest available motors for this type of operation. Our estimation of the bare module cost of the agitator for similar industrial applications is $150.

The specifications for this unit are summarized in the specification sheet on page 65, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Blower/Compressor (B-590)

Blowers are used to increase the pressure of a vapor stream. Blower (B-590) is utilized to produce an increase in pressure of the vapor stream (550) leaving the catalyst removal flash vessel (T-550) from 16.8 to 34.2 psi. Stream (550) undergoes a temperature rise from 194 to 251 °F in the blower. Increasing the pressure of stream (550) is necessary to force the vapor from the catalyst removal flash column (T-550) into the azeotropic distillation column (D-650). The blower operates at an efficiency of 0.72 and moves 16.7 M gpm of vapor to D-650.

The blower is constructed of carbon steel because the feed contains less than 1 PPM of methanesulfonic acid, which is not corrosive enough to harm the blower. The bare module cost, which was approximated from the Ulrich charts was $458 M for both units. A spare will be purchased and installed in case this unit fails. The blower requires 124 kW of electricity to operate.

The specifications for this unit are summarized in the specification sheet on page 66, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Extractive Distillation Column Condenser (C-260)

The condenser of the extractive distillation column condenses vapor components from the top of the column (D-250) and sends them to the reflux accumulator (T-255). The cooling duty of the condenser is 7.87 MM BTU/hr. The flow rate of the vapor distillate is 69.5 lb./hr, which is purged in order to maintain a constant pressure of 257 psi in the reflux accumulator and then sent to an incinerator. The flow rate of the liquid distillate is 6.23 M lb./hr, which is returned to the top of the column. The inlet temperature of the feed is 150 °F and the outlet is 120 °F. The flow rate of cooling water through the condenser is 789 gpm, and its temperature climbs from 90 to 120 °F. The working surface area of the condenser is 2.12 M ft^2, calculated from the logarithmic mean temperature difference, ΔT_{LM}, which is 24.7 °F. The condenser is constructed of carbon steel because the concentration of methanesulfonic acid is less than 1 PPM. The bare module cost of the condenser is $35 M.

The specifications for this unit are summarized in the specification sheet on page 67, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Azeotropic Distillation Column Condenser (C-660)

The condenser of the extractive distillation column condenses vapor components from the top of the column (D-650) and sends them to the reflux accumulator (T-655). The cooling duty of the condenser is 11.9 MM BTU/hr. The flow rate of the vapor distillate is 1.01 M lb./hr, which is purged in order to maintain a constant pressure of 34 psi in the reflux accumulator and then is sent to an incinerator. The flow rate of the liquid

distillate is 6.65 M lb./hr, which is returned to the top of the column. The inlet temperature of the feed is 170 °F and the outlet is 120 °F. The flow rate of cooling water through the condenser is 1.20 M gpm, and its temperature climbs from 90 to 120 °F. The working surface area of the condenser is 2.45 M ft^2, calculated from the logarithmic mean temperature difference, ΔT_{LM}, which is 32.4 °F. The condenser is constructed of carbon steel because the concentration of methanesulfonic acid is less than 1 PPM. The bare module cost of the condenser is $59.4 M.

The specifications for this unit are summarized in the specification sheet on page 68, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Crotonate Removal Column Condenser (C-760)

The condenser of the extractive distillation column condenses vapor components from the top of the column (D-750) and sends them to the reflux accumulator (T-755). The cooling duty of the condenser is 10.5 MM BTU/hr. The flow rate of the vapor distillate is 127 lb./hr, which is purged in order to maintain a constant pressure of 14.7 psi in the reflux accumulator and then sent to an incinerator. The flow rate of the liquid distillate is 10.5 M lb./hr, which is returned to the top of the column. The inlet temperature of the feed is 212.4 °F and the outlet is 211.6 °F. The flow rate of cooling water through the condenser is 1.05 M gpm, and its temperature climbs from 90 to 120 °F. The working surface area of the condenser is 11.7 M ft^2, calculated from the logarithmic mean temperature difference, ΔT_{LM}, which is 6.0 °F. The condenser is

constructed of carbon steel because the concentration of methanesulfonic acid is less than 1 PPM. The bare module cost of the condenser is $149 M.

The specifications for this unit are summarized in the specification sheet on page 69, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Extractive Distillation Column (D-250/1)

The extractive distillation column is used to separate the propadiene impurity from the methyl acetylene reactant in the column feed stream (250). The ratio of methyl acetylene to propadiene must be greater than or equal to 98.1% when fed to the reactor or the catalyst will become inactive. Propadiene and methyl acetylene are very difficult to separate, so a mass separating agent is used. Methanol was selected as the separating agent because it is also used as a reactant later in the process. As calculated by the RADFRAC subroutine in the ASPEN® software, the top and bottom trays are 120.0 and 251 °F respectively. The reflux ratio is 7.04 and the boilup ratio is 2.59. The column has a total of 150 trays, each with an assumed efficiency of 70%, spaced 20 inches apart. The rectifying and stripping sections of the column are split into two separate vessels, each 130' high, because it is unsafe to build a single column that stands higher than 175' tall. The optimal feed tray, which was calculated by the Kirkbride approximation, was 97. The pressure is 257 psi in the condenser and 272 psi in the reboiler. The average inside tray diameter, as calculated by the ASPEN® software, is 4' 8" feet. This column is constructed of carbon steel because no corrosive chemicals are being fed to this column. The distillate stream (280) is mostly propane and it is fed to in the C_3 by-product storage

vessel (T-295), where it is held until it is sent back to the naphtha cracking plant. The bottoms are sent on to the reaction pump (P-270) to be sent to the reactor (R-450).

Comparing three factors minimized the total cost of the unit without sacrificing the necessary purity of the bottoms stream (270). The three factors considered were the cost of the column vessel and trays, the utilities cost, and the effect of methanol flow rate on raw material and increased plant size costs. The methanol recycle flow rates were approximated using the "six-tenths rule". The optimal column was found to have 150 trays with a condenser cooling duty of 7.87 MM BTU/hr and a reboiler heating duty of 10.5 MM BTU/hr.

The reflux accumulator (T-255) for this column was sized as a 6' 11" in diameter, 20' 8' long horizontal vessel. These dimensions are based on the flow rate of vapor to the condenser (C-260), and the assumption that the reflux accumulator has a residence time of 5 minutes when the tank is half full. The area needed for heat transfer was used to size and cost both the condenser and reboiler (K-270). The condenser is a 1-1 shell and tube heat exchanger with a working surface area of 2.12 M ft^2. The reboiler is a kettle type model with an area of 1.05 M ft^2 available for heat exchange. The bare module costs, which were calculated from the Ulrich charts, are \$89 M for the reflux accumulator, \$35 M for the condenser and \$84 M for the reboiler.

The specifications for this unit are summarized in the specification sheet on page 70, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121.

Design calculations for this unit are included in Appendix F.

Azeotropic Distillation Column (D-650)

The azeotropic distillation column separates the methanol solvent from the methyl methacrylate product in stream (590). Methanol and methyl methacrylate form an azeotrope consisting of 95% methanol and 5% methyl methacrylate at 167 °F and 22.0 psi. As calculated by the RADFRAC subroutine in the ASPEN® software, the top and bottom trays of the column are at 120 and 269 °F respectively. The reflux ratio is 3 and the boil-up ratio is 4.11. The column has a total of 11 trays, each with an assumed efficiency of 70%, spaced 20 inches apart. The functional height of the column is 28' 4". The pressure is 34 psi in the condenser (C-660) and 35 psi in the reboiler (K-670). The average tray diameter as calculated by the ASPEN® software is 5' 7". The optimal feed tray, found by the Kirkbride approximation, was 2. The column is constructed of carbon steel because no corrosive chemicals are fed to this column. The distillate, which consists primarily of methanol and MMA, is sent to the methanol recycle stream (680). The bottoms, which contain MMA and a small amount of methyl crotonate, are sent to the crotonate removal distillation column (D-750).

The cost of the unit was minimized by comparing the effect of different numbers of trays on the amount of material sent back through the recycle stream. The composition of the bottoms from the column was kept below 0.1% methanol to ensure that the final product purity of 99.9% could be attained. The "six-tenths rule" was used to estimate the cost associated with changing the flow rate of the recycle stream. This cost was balanced with the utility requirements and cost of the column and trays. The optimal column was found to have 11 trays with a condenser cooling duty of 11.9 MM BTU/hr and a reboiler

heating duty of 7.42 MM BTU/hr. The bare module cost of the entire column, as calculated from the Ulrich charts, is $366 M.

The reflux accumulator (T-655) for this column was sized as 4' 4" in diameter, 10' 10" long horizontal vessel. These dimensions are based on the flow rate of vapor to the condenser, and the assumption that the reflux accumulator has a residence time of 5 minutes when the tank is half full. The area needed for heat transfer was used to size and cost both the condenser and reboiler (K-670). The condenser is a 1-1 shell and tube heat exchanger with a surface area of 2.45 M ft^2. The reboiler is a kettle type model with an area of 742 ft^2 available for heat exchange. The bare module cost as calculated from the Ulrich charts is $42.0 M for the reflux accumulator, $59.4 M for the condenser and $79.7 M for the reboiler.

The specifications for this unit are summarized in the specification sheet on page 71, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Crotonate Removal Distillation Column (D-750)

The crotonate removal distillation column is used to separate the methyl crotonate byproduct from the methyl methacrylate product in stream (690). The column was designed to ensure that methyl methacrylate emerges from the distillate with a purity of 99.9%. As calculated by the RADFRAC subroutine in the ASPEN® software, the top and bottom trays are 212 and 253 °F respectively. The reflux ratio is 4.67 and the boilup ratio is 152.8. The boilup ratio is very high because the separation of MMA and MC is very difficult. The column has a total of 88 trays with an assumed efficiency of 70%, spaced

20 inches apart. The optimal feed tray, which was found by the Kirkbride approximation, was 80. The column is 156' 8" tall, and the average tray diameter calculated by the ASPEN® software is 4' 9". The pressure is 14.7 psi in the condenser (C-760) and 22.6 psi in the reboiler (K-770). This column is constructed of carbon steel because no corrosive chemicals are fed to the column. The distillate is the purified product and it is held in the MMA storage vessel (T-790) until it is sent to the off-site packaging operation. The bottoms are sent to an incinerator for disposal, as there is no profitable market available for methyl crotonate for the quantity produced.

Comparing the cost of various numbers of stages and the corresponding amounts of utilities minimized the cost of the unit. The composition of the distillate from the column was kept above 99.9% methyl methacrylate. The increased cost due to larger utility requirements and larger columns was simultaneously evaluated. The optimal column was found to have 88 trays with a condenser cooling duty of 10.5 MM BTU/hr and a reboiler heating duty of 10.1 MM BTU/hr.

The reflux accumulator for this column (T-755) was sized as a 5' 1" diameter and 15' 2", horizontal vessel. These dimensions are based on the flow rate of vapor to the condenser, and the assumption that the reflux accumulator has a residence time of 5 minutes when the tank is half full. The area required for sufficient heat transfer was used to size and cost the condenser and reboiler. The condenser is a 1-1 shell and tube heat exchanger with a working surface area of 11.7 M ft^2. The reboiler is a kettle type model with an area of 1.01 M ft^2 available for heat exchange. The bare module costs, as calculated from the Ulrich charts, is \$68 M for the reflux accumulator, \$149 M for the condenser, and \$83.9 M for the reboiler.

The specifications for this unit are summarized in the specification sheet on page 72, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Pre-Reaction Heat Exchanger (H-410)

This heat exchanger reduces the temperature of the extractive distillation bottoms stream (290) from 257 °F to 176 °F, which is then fed directly to the carboxymethylation reactor (R-450) via stream (410). The heat exchanger is a 1-1 exchanger. The entire exchanger is constructed from carbon steel. This unit helps to reduce the cooling duty of the reaction heat exchanger (HX-460). The cooling duty is 1.63 MM BTU/hr and the area necessary to cool the reactor feed was calculated to be 89.8 ft^2, assuming a heat transfer coefficient (U) of 150 BTU/hr. The flow rate of the cooling water stream (982) was calculated to be 166 gpm, and as temperature increased from 90 to 122 °F. The bare module cost of this unit is $23.1 M, which was estimated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 73, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Reaction Reflux Heat Exchanger (H-460)

This heat exchanger reduces the temperature of the reactor side stream (460) from 194 °F to 176 °F before returning the cooled stream (465) to the reactor. This exchanger keeps the contents of the reactor at 194 °F. This is a 1-4 heat exchanger, the cooling duty is 12.2 MM BTU/hr, and the area necessary to remove this heat was calculated to be 10.2

M ft^2, assuming a heat transfer coefficient (U) of 150 BTU/hr. The cooling water stream (983) is heated from 90 to 120 °F at a flow rate of 837 gpm in order to achieve the necessary heat removal. The tubes are constructed of Hastelloy-C because methanesulfonic acid, which rapidly corrodes carbon steel, is present in the stream from the reactor. The heat exchanger shell is constructed of carbon steel. The bare module cost, which was estimated using the Ulrich charts, is $358 M.

The specifications for this unit are summarized in the specification sheet on page 74, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Extractive Distillation Reboiler (K-270)

The extractive distillation reboiler vaporizes components in stream (265) from the bottom of the extractive distillation column (D-250) and returns them to the bottom tray of the column through stream (279). The heating duty of the reboiler is 10.5 MM BTU/hr. The inlet temperature of the feed is 197 and the outlet is 251 °F. The flow rate of low-pressure (175-psi) steam is 9.51 M lb./hr, which was calculated from a heat of vaporization of 853 BTU/lb. The working surface area of the reboiler is 1.05 M ft^2. The reboiler is constructed of carbon steel because the concentration of methanesulfonic acid is less than 1 PPM. The bare module cost, which was calculated using the Ulrich charts, is $83.9 M.

The specifications for this unit are summarized in the specification sheet on page 75, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Azeotropic Distillation Column Reboiler (K-670)

The extractive distillation column reboiler vaporizes components in stream (665) from the bottom of the extractive distillation column (D-650) and returns them to the bottom tray of the column through stream (679). The heating duty of the reboiler is 7.42 MM BTU/hr. The inlet temperature of the reboiler is 265 °F and the outlet temperature is 269 °F. The flow rate of low-pressure (175-psi) steam is 8.70 M lb./hr, which was calculated from a heat of vaporization of 853 BTU/lb. The working surface area of the reboiler is 742 M ft^2. The reboiler is constructed of carbon steel because the concentration of methanesulfonic acid is less than 1 PPM. The bare module cost, which was calculated using the Ulrich charts, is $79.7 M.

The specifications for this unit are summarized in the specification sheet on page 76, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Crotonate Removal Distillation Reboiler (K-770)

The extractive distillation column reboiler vaporizes components in stream (765) from the bottom of the extractive distillation column (D-750) and returns them to the bottom tray of the column through stream (779). The heating duty of the reboiler is 10.1 MM BTU/hr. The inlet temperature of the reboiler is 249 °F and the outlet temperature is 253 °F. The flow rate of low-pressure (175-psi) steam is 11.8 M lb./hr, which was calculated from a heat of vaporization of 853 BTU/lb. The working surface area of the reboiler is 1.01 M ft^2. The reboiler is constructed of carbon steel because the

concentration of methanesulfonic acid is less than 1 PPM. The bare module cost, which was calculated using the Ulrich charts, is $83.9 M.

The specifications for this unit are summarized in the specification sheet on page 77, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Catalyst Mixing Tank (M-350)

The catalyst mixer's purpose is to provide adequate space for the blending of the three part catalyst, which consists of methanesulfonic acid, bis(3-chlorophenyl)(2-pyridyl)phosphine and palladium (II) acetate. These three components are fed to the mixer from streams (310), (320), and (330). The mixer is constructed of carbon steel and lined with Hastelloy-C to prevent corrosion. The mixer encapsulates 1.52 ft^3, and measures 2' 7" high by 10" in diameter. The catalyst mixer agitator (A-350) facilitates the mixing. The mixer is built to withstand pressures up to 49.7 psi and temperatures up to 127 ^{o}F. The mixer is used monthly to make a new batch of catalyst feed for the system. The bare module cost is $5 M, which was calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 78, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Inhibitor Mixing Tank (M-810)

The inhibitor mixer's purpose is to provide adequate space for the melting of the polymerization inhibitor, 4-methoxyphenol. The mixer is constructed of carbon steel. The mixer encapsulates 3.7 ft^3, and measures 4' 3" high by 1' 1" in diameter. The inhibitor mixer agitator (A-850) facilitates the mixing. The mixer is built to withstand pressures up to 49.7 psi and temperatures up to 200 °F. The mixer is used continuously to feed inhibitor into the system. The bare module cost is $2 M, which was calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 79, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

C_3 Feed Pump (P-110)

This pump increases the pressure of stream (110) from 175 psi to 327 psi and feeds the isomerization reactor (R-150) through stream (150). Stream (110) has a flow rate of 46.5 gpm. The pump, which is a centrifugal, single-stage, single-suction model that is constructed of carbon steel, has an efficiency of 0.429. The pump consumes 7.14 kW of electricity. A spare pump is purchased and installed in case this unit fails. The bare module cost is $115 M for both pumps, which was estimated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 80, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Methanol Feed Pump (P-210)

This pump increases the pressure of stream (210) from 14.7 psi to 25.0 psi and feeds the methanol recycle, which is sent to the methanol extraction feed pump (P-230) through stream (230). Stream (210) has a flow rate of 11.3 gpm. The pump, which is a reciprocating, metering plunger model that is constructed of carbon steel, has an efficiency of 0.296. The pump consumes 745 W of electricity, even though the actual work necessary to pump this amount of material is smaller. A spare pump is purchased and installed in case this unit fails. The bare module cost is $16 M for both pumps, which was estimated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 81, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Methanol Extraction Feed Pump (P-230)

This pump increases the pressure of stream (230) from 29.4 psi to 257 psi and feeds to the extractive distillation column (D-250) through stream (250). Stream (230) has a flow rate of 28.7 gpm. The pump, which is a centrifugal, single-stage, single-suction model that is constructed of carbon steel has an efficiency of 0.355. The pump consumes 8.01 kW of electricity. A spare pump is purchased and installed in case this unit fails. The bare module cost is $61 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 82, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Extractive Distillation Reflux Pump (P-255)

This pump displaces fluid from the reflux accumulator (T-255) to the extractive distillation column (D-250) through stream (259). Stream (259) has a flow rate of 126 gpm. The pump, which is a rotary gear model that is constructed of carbon steel, has an assumed efficiency of 0.8. The pump consumes 745 W of electricity, even though the actual work necessary to pump this amount of material is smaller. A spare pump is purchased and installed in case this unit fails. The bare module cost is $16 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 83, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Extractive Distillation Bottoms Pump (P-270)

This pump increases the pressure of stream (275) from 272 psi to 880 psi and feeds the pre-reaction heat exchanger (H-410) through stream (290). Stream (275) has a flow rate of 55.7 gpm. The pump, which is a rotary gear model that is constructed of carbon steel, has an efficiency of 0.456. The pump consumes 32.4 kW of electricity. A spare pump is purchased and installed in case this unit fails. The bare module cost is $196 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 84, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Extractive Distillation Distillate Pump (P-280)

This pump displaces the contents of stream (255) from the reflux accumulator (T-255) to the C_3 byproduct storage tank (T-295) through stream (280). Stream (255) has a flow rate of 31.4 gpm. The pump, which is a centrifugal, single-stage, single-suction model that is constructed of carbon steel has an assumed efficiency of 0.8. The pump consumes 745 W of electricity, even though the actual work necessary to pump this amount of material is smaller. A spare pump is purchased and installed in case this unit fails. The bare module cost is $16 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 85, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Catalyst Batch Feed Pump (P-350)

This pump displaces the contents of the catalyst mixing tank (M-350) to the catalyst reactor feed pump (P-390). The pump, which is operated once a month, has a flow rate of 0.49 gpm. The pump, which is a reciprocating, metering diaphragm model that is constructed of Hastelloy-C has an assumed efficiency of 0.8. The pump consumes 745 W of electricity, even though the actual work necessary to pump this amount of material

is smaller. A spare pump is purchased and installed in case this unit fails. The bare module cost is $61 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 86, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Catalyst Reactor Feed Pump (P-390)

This pump increases the pressure of stream (595) from 16.8 psi to 880 psi and feeds the carboxymethylation reactor (R-450) through stream (395). Stream (595) has a flow rate of 1.58 gpm. The pump, which is a reciprocating, metering plunger model that is constructed of Hastelloy-C has an efficiency of 0.296. The pump consumes 2.02 kW of electricity. A spare pump is purchased and installed in case this unit fails. The bare module cost is $394 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 87, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Reactor Reflux Pump (P-450)

This pump increases the pressure of stream (465) from 870 psi to 881 psi and feeds the reactor heat exchanger (H-460) through stream (459). Stream (465) has a flow rate of 1.11 M gpm. The pump, which is a reciprocating, multicylinder plunger model that is constructed of Hastelloy-C has an assumed efficiency of 0.5. The pump consumes 10.7 kW of electricity. A spare pump is purchased and installed in case this unit fails. The

bare module cost is $1.63 MM for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 88, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Azeotropic Distillation Reflux Pump (P-655)

This pump displaces the contents of the azeotropic distillation reflux accumulator (T-655) to the azeotropic distillation column (D-650) through stream (659). The pump has a flow rate of 67.3 gpm. The pump, which is a rotary, screw model that is constructed of carbon steel has an assumed efficiency of 0.8. The pump consumes 745 W of electricity, even though the actual work necessary to pump this amount of material is smaller. A spare pump is purchased and installed in case this unit fails. The bare module cost is $16 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 89, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Azeotropic Distillation Distillate Pump (P-680)

This pump increases the pressure of stream (655) from 34 psi to 44 psi and feeds the methanol extraction feed pump (P-230) through recycle stream (680). Stream (655) has a flow rate of 17.5 gpm. The pump, which is a reciprocating, metering plunger model that is constructed of carbon steel with an efficiency of 0.296. The pump consumes 745

W of electricity, even though the actual work necessary to pump this amount of material is smaller. A spare pump is purchased and installed in case this unit fails. The bare module cost is $16 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 90, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Crotonate Removal Reflux Pump (P-755)

This pump displaces the contents of the crotonate removal reflux accumulator (T-755) to the crotonate removal distillation column (D-750) through stream (759). The pump has a flow rate of 71.8 gpm. The pump, which is a rotary screw model that is constructed of carbon steel has an assumed efficiency of 0.8. The pump consumes 745 W of electricity, even though the actual work necessary to pump this amount of material is smaller. A spare pump is purchased and installed in case this unit fails. The bare module cost is $16 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 91, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Crotonate Removal Bottoms Pump (P-770)

This pump increases the pressure of stream (775) from 23.4 psi to 25.0 psi and feeds stream (798). Stream (775) has a flow rate of 1.14 gpm. The pump, which is a centrifugal multistage model that is constructed of carbon steel has an efficiency of

0.296. The pump consumes 745 W of electricity, even though the actual work necessary to pump this amount of material is smaller. A spare pump is purchased and installed in case this unit fails. The bare module cost is $16 M for both pumps, which was estimated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 92, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Crotonate Removal Distillate Pump (P-780)

This pump increases the pressure of stream (755) from 14.7 psi to 25.0 psi and feeds the MMA product storage tank (T-790) through stream (780). Stream (755) has a flow rate of 29.8 gpm. The pump, which is a reciprocating, metering plunger model that is constructed of carbon steel has an efficiency of 0.36. The pump consumes 745 W of electricity, even though the actual work necessary to pump this amount of material is smaller. A spare pump is purchased and installed in case this unit fails. The bare module cost is $16 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 93, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Inhibitor – Crotonate Removal Feed Pump (P-810A)

This pump increases the pressure of stream (810-A) from 14.7 psi to 25.0 psi and feeds the crotonate removal reflux inhibitor spray (S-755) through stream (815-A).

Stream (810-A) has a flow rate of 0.0014 gpm. The pump, which is a horizontal inline model that is constructed of carbon steel has an efficiency of 0.296. The pump consumes 745 W of electricity, even though the actual work necessary to pump this amount of material is smaller. A spare pump is purchased and installed in case this unit fails. The bare module cost is $16 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 94, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Inhibitor – Azeotropic Distillation Feed Pump (P-810B)

This pump increases the pressure of stream (810-B) from 14.7 psi to 34.0 psi and feeds the azeotropic reflux inhibitor spray (S-655) through stream (815-B). Stream (810-B) has a flow rate of 0.001 gpm. The pump, which is a horizontal inline model that is constructed of carbon steel has an efficiency of 0.296. The pump consumes 745 W of electricity, even though the actual work necessary to pump this amount of material is smaller. A spare pump is purchased and installed in case this unit fails. The bare module cost is $16 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 95, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Inhibitor – Reactor Feed Pump (P-810C)

This pump increases the pressure of stream (810-C) from 14.7 psi to 880 psi and feeds the reactor inhibitor spray (S-450) through stream (815-C). Stream (810-C) has a flow rate of 0.00048 gpm. The pump, which is a horizontal inline model that is constructed of carbon steel has an efficiency of 0.296. The pump consumes 745 W of electricity, even though the actual work necessary to pump this amount of material is smaller. A spare pump is purchased and installed in case this unit fails. The bare module cost is $16 M for both pumps, which was calculated using the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 96, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Isomerization Reactor (R-150)

This reactor, shown in Figure 5 below, converts propadiene to methyl acetylene over a fixed bed of potassium carbonate catalyst on γ alumina. For each mole of propadiene consumed one mole of methyl acetylene is produced as can be seen from the reaction formula.

$$H_2C{=}C{=}CH_2 \rightarrow H_3C\text{-}C{\equiv}CH$$

This reaction occurs in the liquid phase and is most selective for methyl acetylene at lower temperatures and pressures. The reaction is exothermic and chilled water is used to remove the 137 M BTU/hr generated, keeping the reactor between 77 and 87 °F. The inlet pressure to the reactor is 326 psi and the pressure drop was calculated at 69.4 psi, making the outlet pressure 257 psi. The flow rate of feed from stream (150) is 12.4 M

lb./hr composed of 25% methyl acetylene, 25% propadiene and 50% propane with trace amounts of propylene. The reactor converts 80% of the PD to MA. The outlet flow rate to stream (190) is 12.4 M lb./hr, consisting of 45 % methyl acetylene, 5 % propadiene and 50% unreacted propane and propylene.

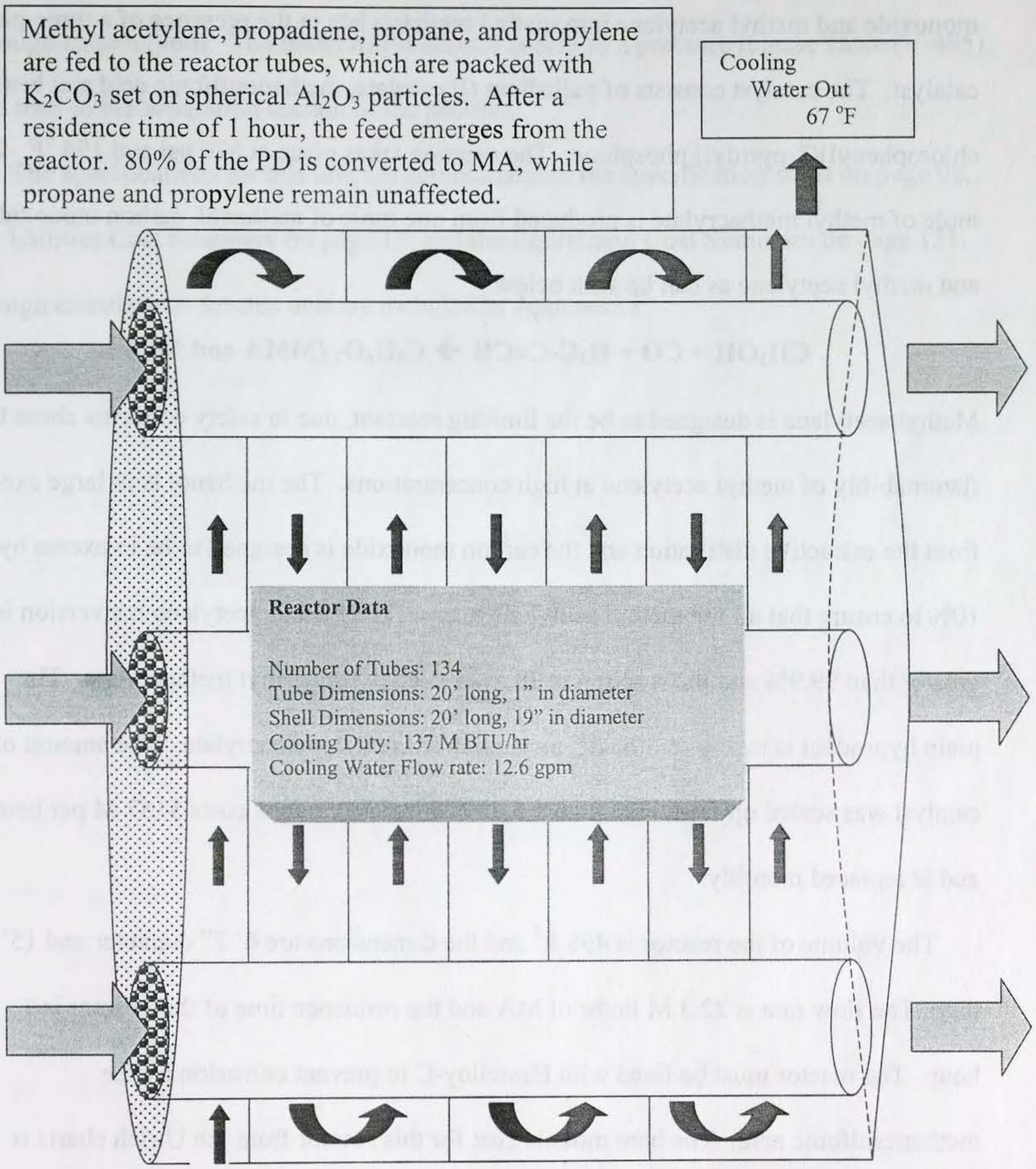
The reactor is a 20-foot long, 4-1 heat exchanger. The reactants flow through 134 packed tubes of 1" outside diameter on a triangular 1¼" pitch. The baffle spacing is 30". The residence time of the reactor is assumed to be 1 hour, corresponding to the space velocity of 10 L feed / L reactor hr given in U.S. patent number 5,081,286. The inside diameter of the reactor shell is 19". The reactor is made of carbon steel, because the reactants are not corrosive. The surface area calculated was 2260 ft^2, assuming an overall heat transfer coefficient (U) of 150 BTU/hr. To maintain the temperature of the reactor below 87 °F, 12.6 gpm of chilled water is heated from 45 to 67 °F. Cooling this chilled water requires 11.4 tons of refrigeration at 32 °F. The amount of catalyst was scaled up from U.S. patent 5,719,313. A spare reactor is purchased to allow the catalyst to be replaced without shutting down the plant every six months because the cost of shutting the plant down far outweighs the cost of purchasing a second reactor. The void fraction of the catalyst was assumed to be 0.45. The outlet is fed via stream (190) directly to the extractive distillation column (D-250/1).

The bare module cost of one heat exchanger design with these specifications is $186 M, which was calculated from the Ulrich charts. The total cost of both reactors is $336 M. The cost of the catalyst is $11.5 M per batch and the catalyst is replaced biannually.

The specifications for this unit are summarized in the specification sheet on page 97, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Figure 5: Isomerization Unit Schematic

(not to scale)



Carboxymethylation Reactor (R-450)

This stirred tank reactor, shown below in Figure 6, converts methanol, carbon monoxide and methyl acetylene into methyl methacrylate in the presence of a three-part catalyst. The catalyst consists of palladium (II) acetate, methanesulfonic acid and bis(3-chlorophenyl)(2-pyridyl) phosphine. The reaction takes place at 870 psi and 194 °F. One mole of methyl methacrylate is produced from one mole of methanol, carbon monoxide, and methyl acetylene as can be seen below.

$$CH_3OH + CO + H_3C\text{-}C{\equiv}CH \rightarrow C_5H_8O_2 \text{ (MMA and MC)}$$

Methyl acetylene is designed to be the limiting reactant, due to safety concerns about the flammability of methyl acetylene at high concentrations. The methanol is in large excess from the extractive distillation and the carbon monoxide is designed to be in excess by 10% to ensure that all the methyl acetylene reacts. The methyl acetylene conversion is greater than 99.9% and the reaction is 98.5% selective for methyl methacrylate. The main byproduct is methyl crotonate, an isomer of methyl methacrylate. The amount of catalyst was scaled up from U.S. patent 5,719,313. The catalyst costs $157 M per batch and is replaced monthly.

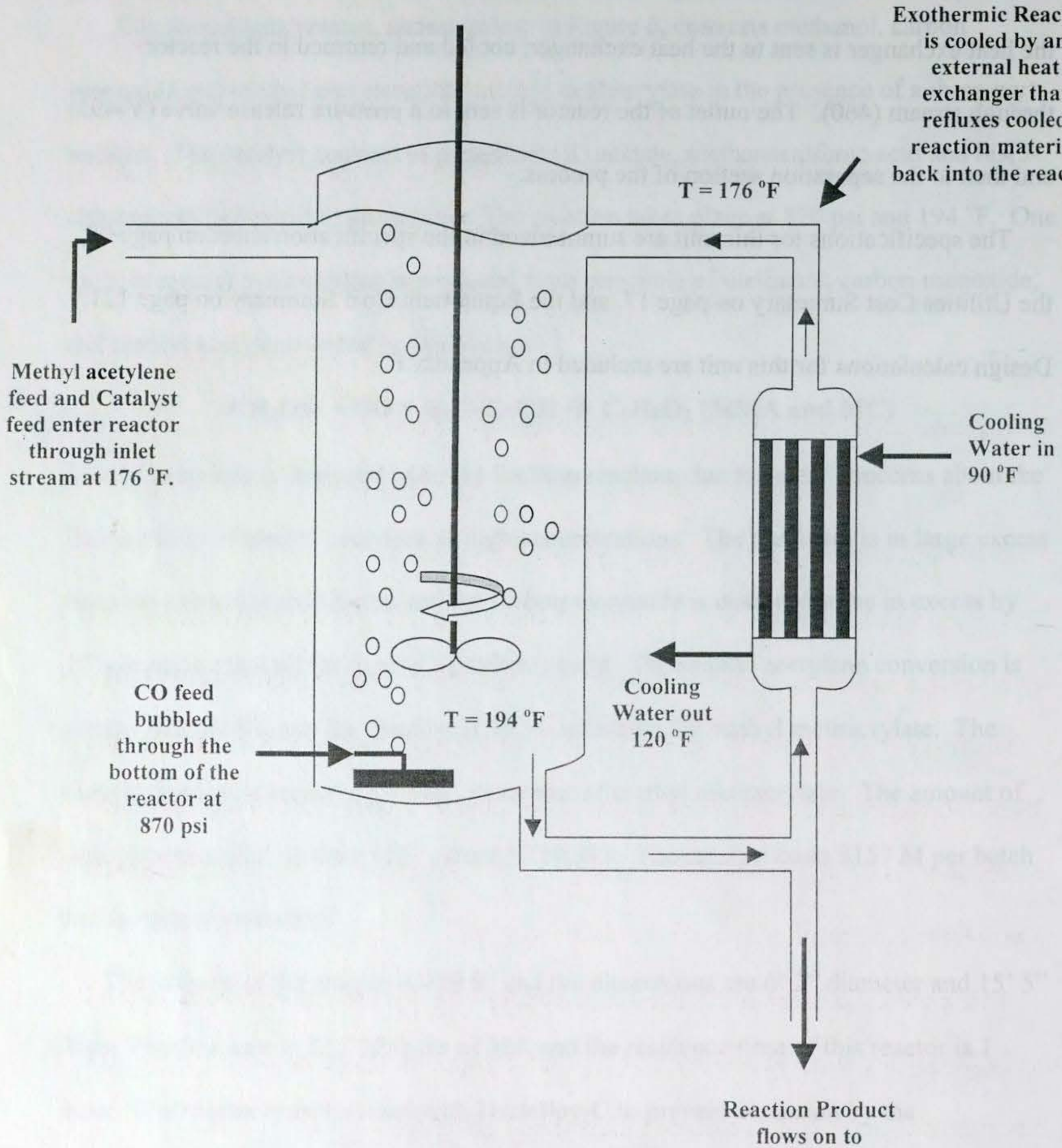
The volume of the reactor is 458 ft^3 and the dimensions are 6' 2" diameter and 15' 5" high. The flow rate is 22.3 M lb./hr of MA and the residence time of this reactor is 1 hour. The reactor must be lined with Hastelloy-C to prevent corrosion by the methanesulfonic acid. The bare module cost for this reactor from the Ulrich charts is $1.01 MM. The reactor mixer agitator (A-450) facilitates mixing in the vessel. The design pressure of the vessel is 985 psi and the design temperature is 244 °F.

This reaction is highly exothermic, generating 12.2 MM BTU/hr. The reactor is cooled by the reactor heat exchanger (H-460). A fraction of the reactor effluent is sent to the heat exchanger is sent to the heat exchanger, cooled and returned to the reactor through stream (460). The outlet of the reactor is sent to a pressure release valve (V-495) and then to the separation section of the process.

The specifications for this unit are summarized in the specification sheet on page 98, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Figure 6: Carboxymethylation Reactor Schematic

(not to scale)



Reactor Inhibitor Spray (S-450)

The purpose of a spray unit is to distribute the 4-methoxyphenol polymerization inhibitor to vessels containing methyl methacrylate. The reactor inhibitor feed pump (P-810C) feeds the inhibitor to the reactor (R-450) through the reactor spray. The flow rate to the reactor spray is 0.00048 gpm, which will provide a concentration of 10 PPM in the reactor to prevent polymerization of the methyl methacrylate.

The specifications for this unit are summarized in the specification sheet on page 99, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Azeotropic Distillation Reflux Inhibitor Spray (S-655)

The purpose of a spray unit is to distribute the 4-methoxyphenol polymerization inhibitor to vessels containing methyl methacrylate. The azeotropic distillation inhibitor feed pump (P-810B) feeds the inhibitor to the azeotropic distillation reflux accumulator (T-655) through the azeotropic distillation reflux inhibitor spray. The flow rate to the reactor spray is 0.001 gpm, which will provide a concentration of 10 PPM in the reactor to prevent polymerization of the methyl methacrylate.

The specifications for this unit are summarized in the specification sheet on page 100, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Crotonate Removal Reflux Inhibitor Spray (S-755)

The purpose of a spray unit is to distribute the 4-methoxyphenol polymerization inhibitor to vessels containing methyl methacrylate. The crotonate removal inhibitor feed pump (P-810A) feeds the inhibitor to the crotonate removal reflux accumulator (T-755) through the crotonate removal reflux inhibitor spray. The flow rate to the reactor spray is 0.0014 gpm, which will provide a concentration of 10 PPM in the reactor to prevent polymerization of the methyl methacrylate.

The specifications for this unit are summarized in the specification sheet on page 101, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

C_3 Storage Tank (T-110)

This tank provides ample space for the C_3 feed to remain before it enters the process through stream (110). The tank is designed to hold 1 day worth of reactant because there is such a large amount of C_3 feed that flows through the system. The vessel is designed as a vertical bullet and is constructed from carbon steel because no corrosive chemicals are stored in this tank. The tank measures 47' 2" high by 15' 9" in diameter, encapsulating 9.17 M ft^3. The minimum thickness of this tank is calculated to be 0.53 in, and it must be built to withstand temperatures up to 127 ^{o}F and pressures up to 210 psi. The bare module cost of this tank is $240 M, as calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 102, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Methanol Storage Tank (T-210)

This tank provides ample space for the methanol feed to remain before it enters the process through stream (210). The tank is designed to hold 7 days worth of reactant. The vessel is designed as a vertical cone roof and is constructed from carbon steel because no corrosive chemicals are stored in this tank. The tank measures 56' 7" high by 18' 10" in diameter, encapsulating 15.8 M ft^3. The minimum thickness of this tank is calculated to be 0.53 in, and it must be built to withstand temperatures up to 127 ^oF and pressures up to 49.7 psi. The bare module cost of this tank is $39 M, as calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 103, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Extraction Distillation Reflux Accumulator (T-255)

This tank provides ample space for the distillate from the extractive distillation column (D-250) to remain before it is refluxed back to the column through stream (259) and sent off as distillate through stream (280). The tank is designed to hold 5 minutes worth of reflux, according to a process design heuristic given by Seader, Seider, and Lewin. The vessel is designed as a horizontal bullet and is constructed from carbon steel because no corrosive chemicals are stored in this tank. The tank measures 20' 8" long by 6' 11" in diameter, encapsulating 766 ft^3. The minimum thickness of this tank is calculated to be 0.53 in, and it must be built to withstand temperatures up to 170 ^oF and

pressures up to 282.2 psi. The bare module cost of this tank is $89 M, as calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 104, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

C_3 Byproduct Storage Tank (T-295)

This tank provides ample space for the C_3 byproduct to remain before it is returned to the naphtha cracking plant. The tank is designed to hold 1 day's worth of byproduct because the supplier is located next to the plant. The vessel is designed as a vertical bullet and is constructed from carbon steel because no corrosive chemicals are stored in this tank. The tank measures 41' 2" high by 13' 9" in diameter, encapsulating 6.1 M ft^3. The minimum thickness of this tank is calculated to be 0.53 in, and it must be built to withstand temperatures up to 127 °F and pressures up to 49.7 psi. The bare module cost of this tank is $174 M, as calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 105, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Palladium Acetate Storage Tank (T-310)

This tank provides ample space for the palladium acetate catalyst feed to remain before it enters the catalyst mixer (M-350). The tank is designed to hold 30 days worth of catalyst because the catalyst is replaced every month. The vessel is designed as a

vertical hopper bin and is constructed from carbon steel because no corrosive chemicals are stored in this tank. The tank measures 3' 3" high by 1' 1" in diameter, encapsulating 3 ft^3. The minimum thickness of this tank is calculated to be 0.4 in, and it must be built to withstand temperatures up to 127 °F and pressures up to 49.7 psi. The bare module cost of this tank is $2 M, as calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 106, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

BCPP Phosphine Storage Tank (T-320)

This tank provides ample space for the phosphine component of the catalyst to remain before it enters the catalyst mixer (M-350). The tank is designed to hold 30 days worth of catalyst because the catalyst is replaced every month. The vessel is designed as a vertical cone roof and is constructed from carbon steel because no corrosive chemicals are stored in this tank. The tank measures 21' high by 7' in diameter, encapsulating 811 ft^3. The minimum thickness of this tank is calculated to be 0.53 in, and it must be built to withstand temperatures up to 127 °F and pressures up to 49.7 psi. The bare module cost of this tank is $10 M, as calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 107, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Methanesulfonic Acid Storage Tank (T-330)

This tank provides ample space for the methanesulfonic acid to remain before it enters the catalyst mixer (M-350). The tank is designed to hold 30 days worth of catalyst because the catalyst is replaced every month. The vessel is designed as a vertical cone roof and is constructed from carbon steel with glass lining to prevent corrosion of the storage vessel. The tank measures 13' high by 4' 4" in diameter, encapsulating 191 ft^3. The minimum thickness of this tank is calculated to be 0.67 in, and it must be built to withstand temperatures up to 127 ^oF and pressures up to 49.7 psi. The bare module cost of this tank is \$13 M, as calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 108, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Catalyst Waste Storage Tank (T-395)

This tank provides ample space for the catalyst waste to remain before it is returned to the supplier. The tank is designed to hold 30 days worth of catalyst because the catalyst is disposed of monthly. The vessel is designed as a vertical cone roof and is constructed from carbon steel with glass lining to prevent corrosion of the storage vessel. The tank measures 2' 5" high by 10" in diameter, encapsulating 1.2 ft^3. The minimum thickness of this tank is calculated to be 0.6 in, and it must be built to withstand temperatures up to 127 ^oF and pressures up to 49.7 psi. The bare module cost of this tank is \$5 M, as calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 109, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Catalyst Flash Column (T-550)

The catalyst flash column separates the acid catalyst from the reaction products and excess reactants in stream (490). The flash operates at 16.8 psi and 194 °F. The flash column pressure is chosen so that the vapor fraction leaving the flash through stream (550) contains less than 1 PPM catalyst. This prevents a corrosive amount of methanesulfonic acid from entering downstream units. The flash vessel is fabricated from carbon steel lined with Hastelloy-C. The flash vessel is designed for a residence time of 10 minutes. The volume of the vessel is 10,700 ft^3, and is 44' high by 18' in diameter. The design pressure is 67.5 psi and the design temperature is 244 °F. The bare module cost, as estimated from the Ulrich charts, is $2.07 MM.

The specifications for this unit are summarized in the specification sheet on page 110, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Azeotropic Distillation Reflux Accumulator (T-655)

This tank provides ample space for the distillate from the azeotropic distillation column (D-650) to remain before it is recycled back to the column through stream (659) and sent off as distillate through stream (680). The tank is designed to hold 5 minutes worth of reflux, according to a process design heuristic given by Seader, Seider, and

Lewin. The vessel is designed as a horizontal process vessel and is constructed from carbon steel because no corrosive chemicals are stored in this tank. The tank measures 10' 10" long by 4' 4" in diameter, encapsulating 79.2 ft^3. The minimum thickness of this tank is calculated to be 0.47 in, and it must be built to withstand temperatures up to 170 ^oF and pressures up to 69 psi. The bare module cost of this tank is \$42 M, as calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 111, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Crotonate Removal Reflux Accumulator (T-755)

This tank provides ample space for the distillate from the crotonate removal distillation column (D-750) to remain before it is recycled back to the column through stream (759) and sent off as distillate through stream (780). The tank is designed to hold 5 minutes worth of reflux, according to a process design heuristic given by Seader, Seider, and Lewin. The vessel is designed as a horizontal process vessel and is constructed from carbon steel because no corrosive chemicals are stored in this tank. The tank measures 15' 2" long by 5' 1" in diameter, encapsulating 305 ft^3. The minimum thickness of this tank is calculated to be 0.53 in, and it must be built to withstand temperatures up to 262 ^oF and pressures up to 49.7 psi. The bare module cost of this tank is \$68 M, as calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 112, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Methyl Methacrylate Storage Tank (T-790)

This tank provides ample space for the methyl methacrylate product to remain before it is sent to the off-site packaging operation. The tank is designed to hold 30 days worth of reactant because the product is shipped to the buyer every month. The vessel is designed as a vertical cone roof tank and is constructed from carbon steel because no corrosive chemicals are stored in this tank. The tank measures 125' high by 41' 9" in diameter, encapsulating 172 M ft^3. The minimum thickness of this tank is calculated to be 0.53 in for rigidity, even though the actual minimum thickness will be much greater due to the massive size of the tank. The vessel must be built to withstand temperatures up to 127 °F and pressures up to 49.7 psi. The bare module cost of this tank is $194 M, as calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 113, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Inhibitor Storage Tank (T-810)

This tank provides ample space for the 4-methoxyphenol inhibitor to remain before it enters the inhibitor mixer (M-810). The tank is designed to hold 30 days worth of inhibitor because there is such a small amount of inhibitor that flows through the system.

The vessel is designed as a vertical hopper bin and is constructed from carbon steel because no corrosive chemicals are stored in this tank. The tank measures 5' 8" high by 1' 11" in diameter, encapsulating 16 ft^3. The minimum thickness of this tank is calculated to be 0.4 in, and it must be built to withstand temperatures up to 127 ^oF and pressures up to 49.7 psi. The bare module cost of this tank is $2 M, as calculated from the Ulrich charts.

The specifications for this unit are summarized in the specification sheet on page 114, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Steam Furnace (U-910)

The steam furnace produces low pressure steam for other units in the plant. The demand for low pressure steam is 27 M lb/hr throughout the plant. The bare module cost for the upgrade of existing steam furnace facilities to accommodate this additional demand is $1.62 MM.

The specifications for this unit are summarized in the specification sheet on page 115, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Cooling Tower (U-920)

The cooling tower produces cooling water for other units in the plant. The demand for cooling water is 2.1 M lb/hr throughout the plant. The bare module cost for the

upgrade of existing cooling tower facilities to accommodate this additional demand is $206 M.

The specifications for this unit are summarized in the specification sheet on page 116, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Refrigerator (U-930)

The refrigerator produces chilled water for other units in the plant. The demand for chilled water is 11.4 M lb/hr throughout the plant. The bare module cost for the upgrade of existing refrigerator facilities to accommodate this additional demand is $16 M.

The specifications for this unit are summarized in the specification sheet on page 117, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Incinerator (None)

The incinerator disposes of unwanted byproducts and incondensible vapors produced by other units in the plant. The incinerator is located beyond the battery limit due to higher environmental standards that are imposed on incinerators. The cost of purchasing, operating, and inspecting the incinerator is not justified by the small amount of material that is burned. We estimated the bare module cost for the use of an off-site incinerator over 15 years to be $1 MM.

The specifications for this unit are summarized in the specification sheet on page 118, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F.

Pressure Reduction Valve (V-495 et al.)

This valve reduces pressure in stream (490) between the reactor (R-450) and the flash vessel (T-550) from 880 psi to 17.5 psi. The valve causes a temperature drop in the stream from 194 to 193 °F. The price is estimated to range from $50 to $150 depending on the quotes of particular vendors.

The specifications for this unit, and for other units similar to it, are summarized in the specification sheet on page 119, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. Design calculations for this unit are included in Appendix F. Note that most of the valves in this process are control valves, whose costs are included in the bare module cost of the unit that they are controlling. Detailed design of valves is beyond the scope of this report.

Controller 798 (Z-798 et al.)

Controller 798 maintains the level of the bottoms in the crotonate removal distillation column (D-750). This controller has proportional control. The manipulated variable is the flow rate of stream (780). The set point is 3', which is half the height from the bottom of the column to the first tray. The price is estimated to range from $100-$2000 depending on the quotes of various vendors.

The specifications for this unit are summarized in the specification sheet on page 120, the Utilities Cost Summary on page 17, and the Equipment Cost Summary on page 121. controllers are included in the bare module cost of the unit that they are controlling. Detailed design of controllers is out of the scope of this report.

VII. SPECIFICATION SHEETS

All equations used in the following section were referenced to section XIII, the equations and nomenclature section, with a bracketed number (i.e. [23] refers to equation 23 in the equations and nomenclature section). The equations and nomenclature page also sites the sources from where the equations were taken.

The symbols such as [U] and [SSL] refer to the acronyms given to book titles in the bibliography, (i.e. [U, 57] refers to Ulrich, p.57).

AGITATOR

Identification:
Item: *Catalyst Mixer Agitator*
Item No.: *A-350*
No. Required: *1*
Date: *April 13, 1999*
By: *ABM*

Function: Facilitates dissolution of $Pd(Ac)_2$ and BCPP-Phosphine in MSA.

Operation: Batch

Design Description:

Type: Impeller
Operation: Blending
MOC: Hastelloy-C
Diameter of Tank: 10"

Design Data:

Tip Speed: 10 ft/min [35]
Superficial Velocity: 0.5 ft/sec [35]
Blade distance above bottom: 3.5" [35]
Blade width: 1" [35]

Utilities: 745 W Electricity needed [35]
Controls: Manual

Comments: See Section 300 in process flowsheet and Appendix F
Bare Module Cost: $1,500 (assumed)

AGITATOR

Identification:
Item: *Reactor Agitator*
Item No.: *A-450*
No. Required: *1*
Date: *April 13, 1999*
By: *ABM*

Function: Facilitates reaction of MA with CO, Methanol, and Catalyst

Operation: Continuous

Design Description:

Type: Impeller
Operation: Blending
MOC: Hastelloy-C
Diameter of Tank: 7' 6"

Design Data:

Tip Speed: 10 ft/min [35]
Superficial Velocity: 1.0 ft/sec [35]
Blade distance above bottom: 2' 6" [35]
Blade width: 6" [35]

Utilities: Electricity 4.67 kW [35]
Controls: Automatic

Comments: See Section 400 in process flowsheet and Appendix F
Bare Module Cost: $1,500 (assumed)

AGITATOR

Identification:
Item: *Inhibitor Mixer Agitator*
Item No.: *A-850*
No. Required: *1*
Date: *April 13, 1999*
By: *ABM*

Function: Facilitates melting of 4-Methoxyphenol

Operation: Continuous

Design Description:

Type: Impeller
Operation: Blending
MOC: Carbon Steel
Diameter of Tank: 16"

Design Data:

Tip Speed: 10 ft/min [35]
Superficial Velocity: 0.5 ft/sec [35]
Blade distance above bottom: 6" [35]
Blade width: 1" [35]

Utilities: 745 W Electricity needed [35]
Controls: Automatic

Comments: See Section 800 in process flowsheet and Appendix F
Bare Module Cost: $150 (assumed)

BLOWER

Identification: Item: *Blower/Compressor* Date: *April 13, 1999*
Item No.: *B-590*
No. Required: *2* By: *ABM*

Function: Increases pressure of stream 550 from 16.8 psi to 34.2 psi

Operation: Continuous

Design Description:

Type: Rotary
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:

Inlet Pressure:	16.8 psi [32]	Inlet Temperature:	194 °F [32]
Outlet Pressure:	34.2 psi [32]	Outlet Temperature:	251 °F [32]
Feed Volumetric Flowrate:	16,700 gpm [32]		
Efficiency:	0.72 [32]		

Utilities: 124 kW Electricity needed [32]
Controls: None Required

Comments: See Section 500 in process flowsheet and Appendices E&F
Bare Module Cost: $229,000 [20]

CONDENSER

Identification: Item: *Extractive Distillation Column Condenser* Date: *April 13, 1999*
Item No.: *C-260*
No. Required: *1* By: *ABM*

Function: Condenses all vapor components from the top of the column (D-250).

Operation: Continuous

Design Description:		*Vap. Dist*	*Liq. Dist*	*Reflux*	
Quantity (lb/hr):		69.5	6,231	43,870	
Mass Fraction:					
Carbon Monoxide		0.049	930 PPM	931 PPM	
Propylene		0.01	0.009	0.009	
Propane		0.879	0.907	0.907	
Propadiene		0.062	0.077	0.077	
Methyl Acetylene		2 PPM	3 PPM	4 PPM	
Methanol		160 PPM	0.006	1.006	
Methyl Methacrylate		6 PPM	724 PPM	724 PPM	
Methyl Crotonate		8 PPB	2 PPM	2 PPM	
Methanesulfonic Acid		---	trace	trace	
BCPP-phosphine		---	trace	trace	
Palladium Acetate		---	trace	trace	
4-Methoxyphenol		---	trace	trace	
Temperature (°F):		120	120	120	Inlet Temp: 150 °F
Pressure (psi):		257	257	257	

Design Data: Type: 1-1 Shell and Tube fixed head Reflux Ratio: 7.04 [32]
Heat Duty: 7.87 MM BTU/hr [32] Surface Area: 2.12 M ft^2 [7]
ΔT_{LM}: 24.7 °F [6] MOC: Carbon Steel

Utilities: Cooling Water, 789 gpm required [7b]
Controls: Automatic

Comments: See Section 200 in process flowsheet and Appendices E & F
Bare Module Cost: $34,700 [17]

CONDENSER

Identification: Item: *Azeotropic Distillation Column Condenser* Date: *April 13, 1999*
Item No.: *C-660*
No. Required: *1* By: *ABM*

Function: Condenses all vapor components from the top of the column (D-650).

Operation: Continuous

Design Description:	*Vap. Dist*	*Liq. Dist*	*Reflux*	
Quantity (lb/hr):	1,010	6,650	19,950	
Mass Fraction:				
Carbon Monoxide	0.657	0.001	0.001	
Propylene	---	---	---	
Propane	827 PPM	125 PPM	125 PPM	
Propadiene	0.047	0.008	0.008	
Methyl Acetylene	---	---	---	
Methanol	0.191	0.521	0.521	
Methyl Methacrylate	0.104	0.467	0.467	
Methyl Crotonate	51 PPM	0.002	0.002	
Methanesulfonic Acid	trace	831 PPB	831 PPB	
BCPP-phosphine	trace	3 PPM	3 PPM	
Palladium Acetate	trace	83 PPB	83 PPB	
4-Methoxyphenol	trace	20 PPB	20 PPB	
Temperature (^{o}F):	120	120	120	Inlet Temp: 170 ^{o}F
Pressure (psi):	34	34	34	

Design Data: Type: 1-1 Shell and Tube fixed head Reflux Ratio: 3 [32]
Heat Duty: 11.9 MM BTU/hr [32] Surface Area: 2.45 M ft^2 [7]
ΔT_{LM}: 32.4 ^{o}F [6] MOC: Carbon Steel

Utilities: Cooling Water, 1200 gpm required [7b]
Controls: Automatic

Comments: See Section 600 in process flowsheet and Appendices E & F
Bare Module Cost: $59,400 [17]

CONDENSER

Identification: Item: *Crotonate Removal Column Condenser* Date: *April 13, 1999*
Item No.: *C-760*
No. Required: *1* By: *ABM*

Function: Condenses all vapor components from the top of the column (D-750).

Operation: Continuous

Design Description:		*Vap. Dist*	*Liq. Dist*	*Reflux*	
Quantity (lb/hr):		127.0	10,511	49,089	
Mass Fraction:					
Carbon Monoxide		---	---	---	
Propylene		---	---	---	
Propane		trace	trace	trace	
Propadiene		trace	trace	trace	
Methyl Acetylene		---	---	---	
Methanol		0.003	305 PPM	305 PPM	
Methyl Methacrylate		0.997	1	1	
Methyl Crotonate		9 PPB	15 PPB	15 PPB	
Methanesulfonic Acid		---	---	---	
BCPP-phosphine		---	---	---	
Palladium Acetate		---	---	---	
4-Methoxyphenol		41 PPB	11 PPM	11 PPM	
Temperature (°F):		211.6	211.6	211.6	Inlet Temp: 212.4 °F
Pressure (psi):		14.7	14.7	14.7	

Design Data: Type: 1-1 Shell and Tube fixed head Reflux Ratio: 4.67 [32]
Heat Duty: 10.5 MM BTU/hr [32] Surface Area: 11.7 M ft^2 [7]
ΔT_{LM}: 6.0 °F [6] MOC: Carbon Steel

Utilities: Cooling Water, 1050 gpm required [7b]
Controls: Automatic

Comments: See Section 700 in process flowsheet and Appendices E & F
Bare Module Cost: $149,000 [17]

DISTILLATION COLUMN

Identification: Item: *Extractive Distillation Column* Date: *April 13, 1999*
Item No.: *D-250/1*
No. Required: *1* By: *ABM*

Function: Separates propadiene from methylacetylene

Operation: Continuous

Materials Handled:	*Feed*	*Solvent*	*Liq. Dist*	*Vap. Dist*	*Bottoms*
Quantity (lb/hr):	12,400	11,900	6,231	69.5	17,200
Mass Fraction:					
Carbon Monoxide	---	837 PPM	930 PPM	0.049	trace
Propylene	0.005	---	0.009	0.01	trace
Propane	0.519	77 PPM	0.907	0.879	102 PPM
Propadiene	0.048	0.005	0.077	0.062	0.009
Methyl Acetylene	0.429	---	3 PPM	2 PPM	0.448
Methanol	---	0.703	0.006	160 PPM	0.697
Methyl Methacrylate	---	0.290	724 PPM	6 PPM	0.289
Methyl Crotonate	---	0.001	2 PPM	8 PPB	0.001
Methanesulfonic Acid	---	506 PPB	trace	---	348 PPB
BCPP-phosphine	---	2 PPM	trace	---	1 PPM
Palladium Acetate	---	51 PPB	trace	---	trace
4-Methoxyphenol	---	12 PPM	trace	---	7 PPM
Temperature (°F):	87	105	120	120	251
Pressure (psi):	267	257	257	257	272

Design Data:
Number of Trays: 150 Feed Stage: 97 [1]
Reflux Ratio: 7.04 [32] Boilup Ratio: 2.59 [32]
Tray Spacing: 20 in Tray Efficiency: 70% [37]
Functional Height: 2 x 130' Recommended ID: 4' 8" [32]
Reflux accumulator: 6' 11" diameter, 20' 8" high
Material of Construction: Carbon steel vessel, trays and reflux accumulator

Utilities:
Condenser: 789 gpm Cooling Water [7b]
Reboiler: 12.3 M lb/hr 175 # Steam [7a]

Comments: See Section 200 in process flowsheet and Appendices E & F
Bare Module Cost (of all parts): $768,000 [3 & 4]

DISTILLATION COLUMN

Identification: Item: *Azeotropic Distillation Column* Date: *April 13, 1999*
Item No.: *D-650*
No. Required: *1* By: *ABM*

Function: Separates methanol from methyl methacrylate

Operation: Continuous

Materials Handled:	*Feed*	*Liq. Dist*	*Vap. Dist*	*Bottoms*
Quantity (lb/hr):	21,600	6,650	1,010	13,200
Mass Fraction:				
Carbon Monoxide	0.031	0.001	0.657	---
Propylene	---	---	---	---
Propane	81 PPM	125 PPM	827 PPM	trace
Propadiene	0.005	0.008	0.047	trace
Methyl Acetylene	---	---	---	---
Methanol	0.187	0.521	0.191	302 PPM
Methyl Methacrylate	0.767	0.467	0.104	0.200
Methyl Crotonate	0.010	0.002	51 PPM	0.984
Methanesulfonic Acid	5 PPM	831 PPB	trace	7 PPM
BCPP-phosphine	15 PPM	3 PPM	trace	1 PPM
Palladium Acetate	500 PPB	83 PPB	trace	trace
4-Methoxyphenol	19 PPM	20 PPB	trace	63 PPM
Temperature (°F):	241	120	120	269
Pressure (psi):	32	34	34	35

Design Data:
Number of Trays: 11 Feed Stage: 2 [1]
Reflux Ratio: 3 [32] Boilup Ratio: 4.11 [32]
Tray Spacing: 20 in Tray Efficiency: 70% [37]
Functional Height: 28' 4" Recommended ID: 5' 7" [32]
Reflux accumulator: 4' 4" diameter, 10' 10" high
Material of Construction: Carbon steel vessel, trays and reflux accumulator

Utilities: Condenser: 1200 gpm Cooling Water [7b]
Reboiler: 8.7 M lb/hr 175 # Steam [7a]

Comments: See Section 600 in process flowsheet and Appendices E & F
Azeotrope is 95% methanol and 5% MMA in the distillate [IL]

Bare Module Cost (of all parts): $366,000 [3 & 4]

DISTILLATION COLUMN

Identification: Item: *Remove Crotonate Dist. Column* Date: *April 13, 1999*
Item No.: *D-750*
No. Required: *1* By: *ABM*

Function: Separates methyl crotonate from methyl methacrylate

Operation: Continuous

Materials Handled:	*Feed*	*Liq. Dist*	*Vap. Dist*	*Bottoms*
Quantity (lb/hr):	13,200	10,511	127.0	463
Mass Fraction:				
Carbon Monoxide	trace	---	---	---
Propylene	---	---	---	---
Propane	trace	trace	trace	---
Propadiene	trace	trace	trace	---
Methyl Acetylene	---	---	---	---
Methanol	320 PPM	305 PPM	0.003	trace
Methyl Methacrylate	0.984	1	0.997	0.565
Methyl Crotonate	0.015	15 PPB	9 PPB	0.431
Methanesulfonic Acid	7 PPM	---	---	205 PPM
BCPP-phosphine	21 PPM	---	---	615 PPM
Palladium Acetate	700 PPB	---	---	21 PPM
4-Methoxyphenol	63 PPM	11 PPM	41 PPB	0.003
Temperature (°F):	269	212	212	253
Pressure (psi):	25	15	15	23

Design Data:
Number of Trays: 88 Feed Stage: 80 [1]
Reflux Ratio: 4.67 [32] Boilup Ratio: 152.8 [32]
Tray Spacing: 20 in Tray Efficiency: 70% [37]
Functional Height: 156' 8" Recommended ID: 4' 9" [32]
Reflux accumulator: 5' 1" diameter, 15' 2" high
Material of Construction: Stainless Steel Clad vessel & trays; Carbon Steel reflux accumulator

Utilities:
Condenser: 1050 gpm Cooling Water [7b]
Reboiler: 11.8 M lb/hr 175 # Steam [7a]

Comments: See Section 700 in process flowsheet and Appendices E & F
Bare Module Cost (of all parts): $947,000 [3 & 4]

HEAT EXCHANGER

Identification:
Item: *Pre-Reaction Heat Exchanger*
Item No.: *H-410*
No. Required: *1*
Date: *April 13, 1999*
By: *ABM*

Function: Lowers the temperature of stream 290 from 257 to 176 °F

Operation: Continuous

Design Description:

Exchanger Type:	Shell-and-Tube
Number of Tube Passes:	1 [11]
Number of Shell Passes:	1
Material of Construction:	Carbon Steel
Number of Tubes :	70
Length of exchanger :	16 ft
Shell inside diameter :	12 in [8a]
Tube pitch :	triangular 1 1/4 in
Baffle spacing :	10 in [8a]
Tube outside diameter :	3/4 in

Design Data:

Cooling Duty:	1.63 MM BTU/hr
Area for Heat Transfer:	89.8 ft^2 [7]
Stream Temperature In:	257 °F [32]
Stream Temperature Out:	176 °F [32]
Water Temperature In:	90 °F [37]
Water Temperature Out:	120 °F [37]
Heat Transfer Coefficient U:	150 BTU/ °F ft^2 [32]
ΔT LM :	44 °F [6]

Utilities: 166 gpm Cooling Water needed [7b]

Controls: Automatic temperature controller of stream 410, SP = 176 °F

Comments: See Section 400 process flowsheet and Appendix F

Bare Module Cost: $23,100 [17]

HEAT EXCHANGER

Identification: Item: *Reaction Reflux Heat Exchanger* Date: *April 13, 1999*
Item No.: *H-460*
No. Required: *1* By: *ABM*

Function: Lowers the temperature of stream 460 from 194 to 176 °F

Operation: Continuous

Design Description:

Exchanger Type:	Shell-and-Tube
Number of Tube Passes:	4 [11]
Number of Shell Passes:	1
Material of Construction:	Hastelloy-C tubes with Carbon Steel shell
Number of Tubes :	256
Length of exchanger :	20 ft [37]
Shell inside diameter :	34.5 in [8a]
Tube pitch :	triangular 1 1/4 in
Baffle spacing :	30 in [8a]
Tube outside diameter :	1 in

Design Data:

Cooling Duty:	12.2 MM BTU/hr
Area for Heat Transfer:	1020 ft^2 [7]
Stream Temperature In:	194 °F [32]
Stream Temperature Out:	176 °F [32]
Water Temperature In:	90 °F [37]
Water Temperature Out:	120 °F [37]
Heat Transfer Coefficient U:	150 BTU/ °F ft^2 [32]
ΔT LM:	79.9 °F [6]

Utilities: 837 gpm Cooling Water needed [7b]

Controls: Automatic temperature controller of stream 460, SP = 176 °F

Comments: See Section 400 process flowsheet and Appendix F

Bare Module Cost: $358,000 [17]

REBOILER

Identification: Item: *Extractive Distillation Reboiler* Date: *April 13, 1999*
Item No.: *K-270*
No. Required: *1* By: *ABM*

Function: Vaporizes all liquid streams from the bottom of the column D-250

Operation: Continuous

Materials Handled:	*Bottoms*	*Boilup*
Quantity (lb/hr):	17,200	44,500
Mass Fraction:		
Carbon Monoxide	trace	---
Propylene	trace	trace
Propane	102 PPM	304 PPM
Propadiene	0.006	0.016
Methyl Acetylene	0.310	0.765
Methanol	0.483	0.183
Methyl Methacrylate	0.200	0.035
Methyl Crotonate	0.001	39 PPM
Methanesulfonic Acid	348 PPB	trace
BCPP-phosphine	1 PPM	trace
Palladium Acetate	trace	trace
4-Methoxyphenol	7 PPM	4 PPB
Temperature (°F):	251	251
Pressure (psi):	272	272

Design Data:
Type: Kettle
MOC: Carbon Steel
ΔH_{VAP}: 853 BTU/lb [SVN]
Steam Pressure: 175 psia
Heat Flux: 10,000 BTU/ft^2 hr (assumed)
Surface Area: 1.05 M ft^2 [7]
Heat Duty: 10.5 MM BTU/hr [32]
Boilup Ratio: 2.59 [32]

Utilities: Low Pressure Steam, 9.51 M lb/hr required [7b]
Controls: Automatic

Comments: See Section 200 in process flowsheet and Appendices E & F
Bare Module Cost: $83,900 [17]

REBOILER

Identification: Item: *Azeotropic Distillation Reboiler* Date: *April 13, 1999*
Item No.: *K-670*
No. Required: *1* By: *ABM*

Function: Vaporizes all liquid streams from the bottom of the column D-650

Operation: Continuous

Materials Handled:	*Bottoms*	*Boilup*
Quantity (lb/hr):	13,200	54,000
Mass Fraction:		
Carbon Monoxide	---	---
Propylene	---	---
Propane	trace	trace
Propadiene	trace	trace
Methyl Acetylene	---	---
Methanol	302 PPM	0.003
Methyl Methacrylate	0.200	0.035
Methyl Crotonate	0.984	0.987
Methanesulfonic Acid	7 PPM	3 PPB
BCPP-phosphine	1 PPM	trace
Palladium Acetate	trace	trace
4-Methoxyphenol	63 PPM	60 PPB
Temperature (°F):	269	269
Pressure (psi):	35	35

Design Data:
Type: Kettle — Heat Flux: 10,000 BTU/ft^2 hr (assumed)
MOC: Carbon Steel — Surface Area: 742 ft^2 [7]
ΔH_{VAP}: 853 BTU/lb [SVN] — Heat Duty: 7.42 MM BTU/hr [32]
Steam Pressure: 175 psia — Boilup Ratio: 4.11 [32]

Utilities: Low Pressure Steam, 8.7 M lb/hr required [7b]
Controls: Automatic

Comments: See Section 600 in process flowsheet and Appendices E & F
Bare Module Cost: $79,700 [17]

REBOILER

Identification: Item: *Crotonate Removal Reboiler* Date: *April 13, 1999*
Item No.: *K-770*
No. Required: *1* By: *ABM*

Function: Vaporizes all liquid streams from the bottom of the column D-750

Operation: Continuous

Materials Handled:	*Bottoms*	*Boilup*
Quantity (lb/hr):	463	70,700
Mass Fraction:		
Carbon Monoxide	---	---
Propylene	---	---
Propane	---	---
Propadiene	---	---
Methyl Acetylene	---	---
Methanol	trace	trace
Methyl Methacrylate	0.565	0.671
Methyl Crotonate	0.431	0.329
Methanesulfonic Acid	205 PPM	61 PPB
BCPP-phosphine	615 PPM	183 PPB
Palladium Acetate	21 PPM	6 PPB
4-Methoxyphenol	0.003	28 PPM
Temperature (°F):	253	253
Pressure (psi):	23	23

Design Data:
Type: Kettle Heat Flux: 10,000 BTU/ft^2 hr (assumed)
ΔH_{VAP}: 853 BTU/lb [SVN] Surface Area: 1010 ft^2 [7]
Heat Duty: 10.1 MM BTU/hr [32] MOC: Stainless Steel
Steam Pressure: 175 psia Boilup Ratio: 152.8 [32]

Utilities: Low Pressure Steam, 11.8 M lb/hr required [7b]
Controls: Automatic

Comments: See Section 700 in process flowsheet and Appendices E & F
Bare Module Cost: $98,000 [17]

MIXER

Identification:
Item: *Catalyst Mixing Tank*
Item No.: *M-350*
No. Required: *1*
Date: *April 13, 1999*
By: *ABM*

Function: Provides space for adequate blending of catalyst components

Operation: Batch

Design Description:
Vessel Type: Cone roof
MOC: Hastelloy-Lined Carbon Steel

Design Data:
Dimensions: 2' 7" high, 10" in diameter
Volume: 1.52 ft^3
Operating Temperature: 77 °F
Design Temperature: 127 °F [36]
Operating Pressure: 14.7 psi
Design Pressure: 49.7 psi [36]
Frequency of Use: monthly

Utilities: None required
Controls: Manual

Comments: See Section 300 in process flowsheet and Appendix F
Bare Module Cost: $5,000 [3]

MIXER

Identification: Item: *Inhibitor Mixing/Melting Tank* Date: *April 13, 1999*
Item No.: *M-810*
No. Required: *1* By: *ABM*

Function: Provides space for adequate melting of 4-methoxyphenol

Operation: Continuous

Design Description:

Vessel Type: Constant-Stirred Tank
MOC: Carbon Steel
Time between solid refills: 1 week

Design Data: Dimensions: 4' 3" high, 1' 1" in diameter
Volume: 3.70 ft^3

Operating Temperature: 150 °F Design Temperature: 200 °F [36]
Operating Pressure: 14.7 psi Design Pressure: 49.7 psi [36]

Utilities: Electricity, 100 W required
Controls: Manual
Comments: See Section 800 in process flowsheet and Appendix F
Note: 100 W heater assumed, even though the duty is smaller.
Bare Module Cost: $2,000 [3]

PUMP

Identification: Item: *C3 Feed Pump* Date: *April 13, 1999*
Item No.: *P-110*
No. Required: *2* By: *ABM*

Function: Increases pressure of stream 110 from 175 psi to 327 psi

Operation: Continuous

Design Description:
Type: Centrifugal, Single Stage, Single Suction [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:
Inlet Pressure: 175 psi [32]
Outlet Pressure: 327 psi [32]
Feed Volumetric Flowrate: 46.5 gpm [32]
Specific Speed: 20 revolutions $gal^{0.5}$ / $min^{1.5}$ $ft^{0.75}$ (970 rpm) [18a]
Efficiency: 0.429 [32]

Utilities: 7.14 kW Electricity needed [32]
Controls: Automatic

Comments: See Section 100 in process flowsheet and Appendix F
Bare Module Cost: $115,000 [19]

PUMP

Identification: Item: *Methanol Feed Pump* Date: *April 13, 1999*
Item No.: *P-210*
No. Required: *2* By: *ABM*

Function: Increases pressure of stream 210 from 14.7 psi to 25.0 psi

Operation: Continuous

Design Description:

Type: Reciprocating Metering Plunger Pump [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:

Inlet Pressure: 14.7 psi [32]
Outlet Pressure: 25.0 psi [32]
Feed Volumetric Flowrate: 11.3 gpm [32]
Specific Speed: 46.5 revolutions gal / $min^{1.5}$ $ft^{0.75}$ (970 rpm) [18a]
Efficiency: 0.296 [32]

Utilities: 745 W Electricity needed [32]
Controls: Automatic
Comments: See Section 200 in process flowsheet and Appendix F
Note: 1 hp pump assumed, even though the duty is smaller.
Bare Module Cost: $16,000 [19]

PUMP

Identification: Item: *Methanol Extraction Feed Pump* Date: *April 13, 1999*
Item No.: *P-230*
No. Required: *2* By: *ABM*

Function: Increases pressure of stream 230 from 29.4 psi to 257.1 psi

Operation: Continuous

Design Description:

Type: Centrifugal, Single Stage, Single Suction [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:

Inlet Pressure: 29.4 psi [32]
Outlet Pressure: 257.1 psi [32]
Feed Volumetric Flowrate: 28.7 gpm [32]
Specific Speed: 20 revolutions $gal^{0.5}$ / $min^{1.5}$ $ft^{0.75}$ (970 rpm) [18a]
Efficiency: 0.355 [32]

Utilities: 8.01 kW Electricity needed [32]
Controls: Automatic

Comments: See Section 200 in process flowsheet, and Appendix F
Bare Module Cost: $61,000 [19]

PUMP

Identification: Item: *Extractive Distillation Reflux Pump* Date: *April 13, 1999*
Item No.: *P-255*
No. Required: *2* By: *ABM*

Function: Positively displaces liquid reflux from T-255 to D-250

Operation: Continuous

Design Description:

Type: Rotary, Gear [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:

Feed Volumetric Flowrate: 126 gpm [32]
Specific Speed: 20 revolutions gal / $min^{1.5}$ $ft^{0.75}$ (1770 rpm) [18a]
Efficiency: 0.8 (assumed)

Utilities: 745 W Electricity needed [18]
Controls: Automatic
Comments: See Section 200 in process flowsheet
Note: 1 hp pump assumed, even though the duty is smaller.
Bare Module Cost: $16,000 [19]

PUMP

Identification:
Item: *Extractive Distillation Bottoms Pump*
Item No.: *P-270*
No. Required: *2*
Date: *April 13, 1999*
By: *ABM*

Function: Increases pressure of stream 275 from 271.9 psi to 880.0 psi

Operation: Continuous

Design Description:

Type: Rotary, Gear [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:

Inlet Pressure: 271.9 psi [32]
Outlet Pressure: 880.0 psi [32]
Feed Volumetric Flowrate: 55.7 gpm [32]
Specific Speed: 40 revolutions gal / $min^{1.5}$ $ft^{0.75}$ (1770 rpm) [18a]
Efficiency: 0.456 [32]

Utilities: 32.4 kW Electricity needed [32]
Controls: Automatic

Comments: See Section 200 in process flowsheet and Appendix F
Bare Module Cost: $196,000 [19]

PUMP

Identification:
Item: *Extractive Distillation Distillate Pump*
Item No.: *P-280*
No. Required: *2*
Date: *April 13, 1999*
By: *ABM*

Function: Positively displaces distillate from T-255 to T-295

Operation: Continuous

Design Description:

Type: Centrifugal, Single Stage, Single Suction [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:

Feed Volumetric Flowrate: 31.4 gpm [32]
Specific Speed: 20 revolutions gal / $min^{1.5}$ $ft^{0.75}$ (1770 rpm) [18a]
Efficiency: 0.8 (assumed)

Utilities: 745 W Electricity needed [18]
Controls: Automatic
Comments: See Section 200 in process flowsheet and Appendix F
Note: 1 hp pump assumed, even though the duty is smaller.
Bare Module Cost: $16,000 [19]

PUMP

Identification:
Item: *Catalyst Batch Feed Pump*
Item No.: *P-350*
No. Required: *2*
Date: *April 13, 1999*
By: *ABM*

Function: Positively displaces catalyst from M-350 to P-390

Operation: Batch

Design Description:

Type: Reciprocating, Metering Diaphragm [18a]
Orientation: Horizontally mounted
Material of Construction: Hastelloy-C

Design Data:

Feed Volumetric Flowrate: 0.49 gpm [32]
Specific Speed: 100 revolutions gal / $min^{1.5}$ $ft^{0.75}$ (970 rpm) [18a]
Efficiency: 0.8 (assumed)

Utilities: 745 W Electricity needed [18]
Controls: Automatic
Comments: See Section 300 in process flowsheet
Note: 1 hp pump assumed, even though the duty is smaller.
Bare Module Cost: $61,000 [19]

PUMP

Identification: Item: *Catalyst Reactor Feed Pump* Date: *April 13, 1999*
Item No.: *P-390*
No. Required: *2* By: *ABM*

Function: Increases pressure of stream 595 from 16.8 psi to 880.0 psi

Operation: Continuous

Design Description:

Type: Reciprocating, Metering Plunger [18a]
Orientation: Horizontally mounted
Material of Construction: Hastelloy-C

Design Data:

Inlet Pressure: 16.8 psi [32]
Outlet Pressure: 880.0 psi [32]
Feed Volumetric Flowrate: 1.58 gpm [32]
Specific Speed: 10 revolutions gal / $min^{1.5}$ $ft^{0.75}$ (3550 rpm) [18a]
Efficiency: 0.296 [32]

Utilities: 2.02 kW Electricity needed [18]
Controls: Automatic

Comments: See process flowsheet, section 300 and Appendix F
Bare Module Cost: $394,000 [19]

PUMP

Identification:
Item: *Reactor Reflux Pump*
Item No.: *P-450*
No. Required: *2*
Date: *April 13, 1999*
By: *ABM*

Function: Increases pressure of stream 465 from 870.0 psi to 881.0 psi

Operation: Continuous

Design Description:

Type: Reciprocating, Multicylinder Plunger [18a]
Orientation: Horizontally mounted
Material of Construction: Hastelloy-C

Design Data:

Inlet Pressure: 870.0 psi [32]
Outlet Pressure: 881.0 psi [32]
Feed Volumetric Flowrate: 1110 gpm [32]
Specific Speed: 1000 revolutions gal / $min^{1.5}$ $ft^{0.75}$ (4000 rpm) [18a]
Efficiency: 0.5 (assumed)

Utilities: 10.7 kW Electricity needed [18]
Controls: Automatic

Comments: See Section 400 in process flowsheet
Bare Module Cost: $1.63 MM [19]

PUMP

Identification: Item: *Azeotropic Distillation Reflux Pump* Date: *April 13, 1999*
Item No.: *P-655*
No. Required: *2* By: *ABM*

Function: Positively displaces liquid reflux from T-655 to D-650

Operation: Continuous

Design Description:

Type: Rotary, Screw [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:

Feed Volumetric Flowrate: 67.3 gpm [32]
Specific Speed: 550 revolutions gal / $min^{1.5}$ $ft^{0.75}$ (970 rpm) [18a]
Efficiency: 0.8 (assumed)

Utilities: 745 W Electricity needed [18]
Controls: Automatic
Comments: See Section 600 in process flowsheet
Note: 1 hp pump assumed, even though the duty is smaller.
Bare Module Cost: $16,000 [19]

PUMP

Identification: Item: *Azeotropic Distillation Distillate Pump* Date: *April 13, 1999*
Item No.: *P-680*
No. Required: *2* By: *ABM*

Function: Increases pressure of stream 655 from 34.0 psi to 44.0 psi

Operation: Continuous

Design Description:

Type: Reciprocating, Metering Plunger [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:

Inlet Pressure: 34.0 psi [32]
Outlet Pressure: 44.0 psi [32]
Feed Volumetric Flowrate: 17.5 gpm [32]
Specific Speed: 150 revolutions gal / $min^{1.5}$ $ft^{0.75}$ (970 rpm) [18a]
Efficiency: 0.296 [32]

Utilities: 745 W Electricity needed [18]
Controls: Automatic
Comments: See Section 600 in process flowsheet and Appendix F
Note: 1 hp pump assumed, even though the duty is smaller.
Bare Module Cost: $16,000 [19]

PUMP

Identification:
Item: *Crotonate Removal Reflux Pump*
Item No.: *P-755*
No. Required: *2*
Date: *April 13, 1999*
By: *ABM*

Function: Positively displaces liquid reflux from T-755 to D-750

Operation: Continuous

Design Description:
Type: Rotary, Screw [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:
Feed Volumetric Flowrate: 71.8 gpm [32]
Specific Speed: 1050 revolutions gal / $min^{1.5}$ $ft^{0.75}$ (970 rpm) [18a]
Efficiency: 0.8 (assumed)

Utilities: 745 W Electricity needed [18]
Controls: Automatic
Comments: See Section 700 in process flowsheet
Note: 1 hp pump assumed, even though the duty is smaller.
Bare Module Cost: $16,000 [19]

PUMP

Identification: Item: *Crotonate Removal Bottoms Pump* Date: *April 13, 1999*
Item No.: *P-770*
No. Required: *2* By: *ABM*

Function: Increases pressure of stream 775 from 23.4 psi to 25.0 psi

Operation: Continuous

Design Description:

Type: Centrifugal, Multistage [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:

Inlet Pressure: 23.4 psi [32]
Outlet Pressure: 25.0 psi [32]
Feed Volumetric Flowrate: 1.14 gpm [32]
Specific Speed: 80 revolutions gal / $min^{1.5}$ $ft^{0.75}$ (970 rpm) [18a]
Efficiency: 0.296 [32]

Utilities: 745 W Electricity needed [18]
Controls: Automatic
Comments: See Section 700 in process flowsheet and Appendix F
Note: 1 hp pump assumed, even though the duty is smaller.
Bare Module Cost: $16,000 [19]

PUMP

Identification: Item: *Crotonate Removal Distillate Pump* Date: *April 13, 1999*
Item No.: *P-780*
No. Required: *2* By: *ABM*

Function: Increases pressure of stream 755 from 14.7 psi to 25.0 psi

Operation: Continuous

Design Description:

Type: Reciprocating, Metering Plunger [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:

Inlet Pressure: 14.7 psi [32]
Outlet Pressure: 25.0 psi [32]
Feed Volumetric Flowrate: 29.8 gpm [32]
Specific Speed: 500 revolutions gal / $min^{1.5}$ $ft^{0.75}$ (970 rpm) [18a]
Efficiency: 0.36 [32]

Utilities: 745 W Electricity needed [18]
Controls: Automatic
Comments: See Section 700 in process flowsheet and Appendix F
Note: 1 hp pump assumed, even though the duty is smaller.
Bare Module Cost: $16,000 [19]

PUMP

Identification: Item: *Inhibitor - Crotonate Removal Feed Pump* Date: *April 13, 1999*
Item No.: *P-810A*
No. Required: *2* By: *ABM*

Function: Increases pressure of stream 810A from 14.7 psi to 25.0 psi

Operation: Continuous

Design Description:
Type: Process, Horizontal Inline [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:
Inlet Pressure: 14.7 psi [32]
Outlet Pressure: 25.0 psi [32]
Feed Volumetric Flowrate: 0.0014 gpm [32]
Specific Speed: N/A
Efficiency: 0.296 [32]

Utilities: 745 W Electricity needed [18]
Controls: Automatic
Comments: See Section 800 in process flowsheet and Appendix F
Note: 1 hp pump assumed, even though the duty is smaller.
Bare Module Cost: $16,000 [19]

PUMP

Identification:
Item: *Inhibitor - Azeotropic Dist. Feed Pump*
Item No.: *P-810B*
No. Required: *2*
Date: *April 13, 1999*
By: *ABM*

Function: Increases pressure of stream 810B from 14.7 psi to 34.0 psi

Operation: Continuous

Design Description:

Type: Process, Horizontal Inline [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:

Inlet Pressure: 14.7 psi [32]
Outlet Pressure: 34.0 psi [32]
Feed Volumetric Flowrate: 0.001 gpm [32]
Specific Speed: N/A
Efficiency: 0.296 [32]

Utilities: 745 W Electricity needed [18]
Controls: Automatic
Comments: See Section 800 in process flowsheet and Appendix F
Note: 1 hp pump assumed, even though the duty is smaller.
Bare Module Cost: $16,000 [19]

PUMP

Identification: Item: *Inhibitor - Reactor Feed Pump* Date: *April 13, 1999*
Item No.: *P-810C*
No. Required: *2* By: *ABM*

Function: Increases pressure of stream 810C from 14.7 psi to 880.0 psi

Operation: Continuous

Design Description:
Type: Process, Horizontal Inline [18a]
Orientation: Horizontally mounted
Material of Construction: Carbon Steel

Design Data:
Inlet Pressure: 14.7 psi [32]
Outlet Pressure: 880.0 psi [32]
Feed Volumetric Flowrate: 0.00048 gpm [32]
Specific Speed: N/A
Efficiency: 0.296 [32]

Utilities: 745 W Electricity needed [18]
Controls: Automatic
Comments: See Section 800 in process flowsheet and Appendix F
Note: 1 hp pump assumed, even though the duty is smaller.
Bare Module Cost: $16,000 [19]

REACTOR

Identification: Item: *Isomerization Reactor* Date: *April 13, 1999*
Item No.: *R-150*
No. Required: *2* By: *ABM*

Function: Converts Propadiene to Methylacetylene.

Operation: Continuous

Design Description:

Reactor Type:	Packed Bed/Heat Exchanger
Orientation:	Horizontal
Dimensions:	20 ft high, 19" in diameter
Catalyst Type:	Potassium Carbonate on γ Alumina
Material of Construction:	Carbon Steel

Design Data:

Pressure Range:	257 to 317 psi	Conversion:	80% [DY]
Temperature Range:	77 to 87 ^{o}F	Selectivity:	> 99.9 %
Mass Flowrate:	12.4 M lb/hr [32]	Byproducts:	none
Volumetric Flowrate:	374 ft^3/hr	Residence time :	1 hour (assumed)

Heat Exchanger Type :	1-4 shell and tube [11]
Surface Area for heat transfer :	2260 ft^2 [7]
Number of tubes :	134
Tube pitch :	triangular 1 1/4"
Baffle spacing :	30 " [8a]

Utilities: 12.6 gpm Chilled Water needed [7b]
Controls: Automatic

Comments: See Section 100 in process flowsheet and Appendix F
Bare Module Cost (1 reactor): $168,000 [17]

REACTOR

Identification: Item: *Carboxymethylation Reactor* Date: *April 13, 1999*
Item No.: *R-450*
No. Required: *1* By: *ABM*

Function: Converts Methylacetylene, Methanol and Carbon Monoxide to Methyl Methacrylate

Operation: Continuous

Design Description:

Reactor Type: Stirred tank
Orientation: Vertical
Dimensions: 15' 5" high by 6' 2" in diameter
Catalyst Type: Homogeneous solution of MSA, Pd(II)Acetate and Phosphine
MOC: Hastelloy-C lined Carbon Steel

Design Data:

Operating Pressure : 870 psi
Design Pressure: 985 psi [36]
Operating Temperature: 194 °F
Design Temperature: 244 °F [36]

Volumetric Flowrate: 458 ft^3/hr
Mass Flowrate: 22.3 M lb/hr [32]
Residence time : 1 hr [DY]
Conversion: > 99.9 % [DY]
Selectivity: 98.5% MMA [DY]
Byproducts: Methyl Crotonate

Utilities: None required
Controls: Automatic

Comments: See Section 400 in process flowsheet and Appendix F
Bare Module Cost: $1.01 MM [3]

SPRAY

Identification: Item: *Reactor Inhibitor Spray* Date: *April 13, 1999*
Item No.: *S-450*
No. Required: *1* By: *ABM*

Function: Distributes 4-methoxyphenol inhibitor in tank T-450

Operation: Continuous

Design Description:

Purpose: To distribute the polymerization inhibitor throughout the reaction vessel
Orientation: Mounted on inside top of unit
MOC: Hastelloy-C

Design Data:

Operating Temperature: 194 °F
Operating Pressure: 870 psi
Inhibitor Flowrate: 0.26 lb/hr [32]

Utilities: None Required
Controls: Automatic

Comments: See Sections 400 and 800 in process flowsheet and Appendix F
Bare Module Cost: $750 (assumed)

SPRAY

Identification: Item: *Azeotropic Dist. Reflux Inhibitor Spray* Date: *April 13, 1999*
Item No.: *S-655*
No. Required: *1* By: *ABM*

Function: Distributes 4-methoxyphenol inhibitor in tank T-655

Operation: Continuous

Design Description:

Purpose: To distribute the polymerization inhibitor throughout the reflux accumulator
Orientation: Mounted on inside top of unit
MOC: Carbon Steel

Design Data:

Operating Temperature: 120 °F
Operating Pressure: 34 psi
Inhibitor Flowrate: 0.54 lb/hr [32]

Utilities: None Required
Controls: Automatic

Comments: See Sections 600 and 800 in process flowsheet and Appendix F
Bare Module Cost: $75 (assumed)

SPRAY

Identification: Item: *Crotonate Removal Reflux Inhibitor Spray* Date: *April 13, 1999*
Item No.: *S-755*
No. Required: *1* By: *ABM*

Function: Distributes 4-methoxyphenol inhibitor in tank T-755

Operation: Continuous

Design Description:

Purpose: To distribute the polymerization inhibitor throughout the reflux accumulator
Orientation: Mounted on inside top of unit
MOC: Carbon Steel

Design Data:

Operating Temperature: 212 °F
Operating Pressure: 14.7 psi
Inhibitor Flowrate: 0.75 lb/hr [32]

Utilities: None Required
Controls: Automatic

Comments: See Sections 700 and 800 in process flowsheet and Appendix F
Bare Module Cost: $75 (assumed)

TANK

Identification: Item: *C3 Feed Storage Tank* Date: *April 13, 1999*
Item No.: *T-110*
No. Required: *1* By: *ABM*

Function: Stores C3 Feed Stream

Operation: Continuous

Design Description:

Orientation: Vertical Bullet [U] Material of Construction: Carbon Steel
Dimensions: 47' 2" high, 15' 9" in diameter Volume: 9173 ft^3 [22]
Support: Concrete Foundations [37] Minimum Wall Thickness: 0.53 in [37]

Design Data: Hold Up Time: 1 day
Operating Temperature: 77 °F Design Temperature : 127 °F [36]
Operating Pressure: 175 psi Design Pressure : 210 psi [36]

Utilities: None Required
Controls: Automatic

Comments: See Section 100 in process flowsheet and Appendix F
Bare Module Cost: $240,000 [3]

TANK

Identification: Item: *Methanol Storage Tank* Date: *April 13, 1999*
Item No.: *T-210*
No. Required: *1* By: *ABM*

Function: Stores Methanol

Operation: Continuous

Design Description:

Orientation: Vertical Cone Roof [U] Material of Construction: Carbon Steel
Dimensions: 56' 7" high, 18' 10" in diameter Volume: 15800 ft^3 [22]
Support: Concrete Foundations Minimum Wall Thickness: 0.53 in [37]

Design Data: Hold Up Time: 7 days
Operating Temperature: 77 °F Design Temperature : 127 °F [36]
Operating Pressure: 14.7 psi Design Pressure : 49.7 psi [36]

Utilities: None Required
Controls: Automatic

Comments: See Section 200 in process flowsheet and Appendix F
Bare Module Cost: $39,000 [3]

TANK

Identification: Item: *Extraction Distillation Reflux Accumulator* Date: *April 13, 1999*
Item No.: *T-255*
No. Required: *1* By: *ABM*

Function: Stores Condensed Vapor from Extraction Column (D-250)

Operation: Continuous

Design Description:

Orientation: Horizontal Bullet [U] Material of Construction: Carbon Steel
Dimensions: 20' 8" long, 6' 11" in diameter Volume: 766 ft^3 [22]
Support: Concrete Supports [37]
Minimum Wall Thickness: 0.53 in [37]

Design Data: Hold Up Time: 5 min
Operating Pressure: 247.9 psi Design Pressure: 282.2 psi [36]
Operating Temperature: 120 °F Design Temperature: 170 °F [36]

Utilities: None Required
Controls: Automatic
Tolerances:
Comments: See Section 200 in process flowsheet and Appendix F
Bare Module Cost: $89,000

TANK

Identification:
Item: *C3 By-Product Storage Tank*
Item No.: *T-295*
No. Required: *1*
Date: *April 13, 1999*
By: *ABM*

Function: Stores C3 By-Product before returning to supplier

Operation: Continuous

Design Description:

Orientation: Vertical Bullet [U]
Material of Construction: Carbon Steel
Dimensions: 41' 2" high, 13' 9" in diameter
Volume: 6100 ft^3 [22]
Support: Concrete Foundations
Minimum Wall Thickness: 0.53 in [37]

Design Data:
Hold Up Time: 1 day
Operating Temperature: 77 °F
Design Temperature : 127 °F [36]
Operating Pressure: 14.7 psi
Design Pressure : 49.7 psi [36]

Utilities: None Required
Controls: Automatic

Comments: See Section 200 in process flowsheet and Appendix F
Bare Module Cost: $174,000 [3]

TANK

Identification: Item: *Palladium Acetate Storage Tank* Date: *April 13, 1999*
Item No.: *T-310*
No. Required: *1* By: *ABM*

Function: Stores Palladium Acetate

Operation: Batch

Design Description:

Orientation: Vertical Hopper Bin [U] Material of Construction: Carbon Steel
Dimensions: 3' 3" high, 1' 1" in diameter Volume: 3 ft^3 [22]
Support: Legs [37] Minimum Wall Thickness: 0.40 in [37]

Design Data: Hold Up Time: 30 days
Operating Temperature: 77 °F Design Temperature : 127 °F [36]
Operating Pressure: 14.7 psi Design Pressure : 49.7 psi [36]

Utilities: None Required
Controls: Manual

Comments: See Section 300 in process flowsheet and Appendix F
Bare Module Cost: $2,000 [3]

TANK

Identification: Item: *BCPP Phosphine Storage Tank* Date: *April 13, 1999*
Item No.: *T-320*
No. Required: *1* By: *ABM*

Function: Stores BCPP Phosphine

Operation: Batch

Design Description:

Orientation: Vertical Cone Roof [U] Material of Construction: Carbon Steel
Dimensions: 21' high, 7' in diameter Volume: 811 ft^3 [22]
Support: Concrete Supports [37] Minimum Wall Thickness: 0.53 in [37]

Design Data: Hold Up Time: 30 days
Operating Temperature: 77 °F Design Temperature : 127 °F [36]
Operating Pressure: 14.7 psi Design Pressure : 49.7 psi [36]

Utilities: None Required
Controls: Manual

Comments: See Section 300 in process flowsheet and Appendix F
Bare Module Cost: $10,000 [3]

TANK

Identification: Item: *Methanesulfonic Acid Storage Tank* Date: *April 13, 1999*
Item No.: *T-330*
No. Required: *1* By: *ABM*

Function: Stores Methanesulfonic Acid

Operation: Batch

Design Description:

Orientation: Vertical Cone Roof [U] MOC: Carbon Steel Glass Lined
Dimensions: 13' high, 4' 4" in diameter Volume: 191 ft^3 [22]
Support: Concrete Supports [37]
Minimum Wall Thickness: 0.67 in [37]

Design Data: Hold Up Time: 30 days
Operating Temperature: 77 °F Design Temperature : 127 °F [36]
Operating Pressure: 14.7 psi Design Pressure : 49.7 psi [36]

Utilities: None Required
Controls: Manual

Comments: See Section 300 in process flowsheet and Appendix F
Bare Module Cost: $13,000 [3]

TANK

Identification: Item: *Catalyst Waste Storage* Date: *April 13, 1999*
Item No.: *T-395*
No. Required: *1* By: *ABM*

Function: Stores Catalyst Waste Product

Operation: Batch

Design Description:

Orientation: Vertical Cone Roof [U] MOC: Carbon Steel Glass Lined
Dimensions: 2' 5" high, 10" in diameter Volume: 1.2 ft^3 [22]
Support: Legs [37] Minimum Wall Thickness: 0.60 in [37]

Design Data: Hold Up Time: 30 days
Operating Temperature: 77 °F Design Temperature : 127 °F [36]
Operating Pressure: 14.7 psi Design Pressure : 49.7 psi [36]

Utilities: None Required
Controls: Manual

Comments: See Section 300 in process flowsheet and Appendix F
Bare Module Cost: $5.000 [3]

TANK

Identification: Item: *Catalyst Flash Column with Steam Heater* Date: *April 13, 1999*
Item No.: *T-550 & H-550*
No. Required: *1* By: *ABM*

Function: Separate catalyst mixture from other components of stream (490)

Operation: Continuous

Design Description:

Orientation: Vertical Bullet [U] Volume: 137.4 ft^3 [22]
Dimensions: 11' 11" high, 3' 10" in diameter MOC: Hastelloy-C Lined
Support: Concrete Supports [37]
Minimum Wall Thickness: 0.67 in [37]

Design Data: Hold Up Time: 10 min
Operating Temperature: 194 °F Design Temperature: 244 °F
Operating Pressure: 16.8 psi Design Pressure: 51.8 psi

K-Values:

Carbon Monoxide:	274	Methyl Methacrylate:	0.656
Propane:	27.3	Methyl Crotonate:	0.326
Propadiene:	22.0	Methanesulfonic Acid:	3.3E-06
Methanol:	4.56	4-Methoxyphenol:	0.00147

Utilities: Steam: 5390 lb/hr @ 175 psi
Controls: Automatic

Comments: See Section 500 in process flowsheet and Appendix F
Bare Module Cost: $103,000

TANK

Identification: Item: *Azeotropic Distillation Reflux Accumulator* Date: *April 13, 1999*
Item No.: *T-655*
No. Required: *1* By: *ABM*

Function: Stores Condensed Vapor from Azeotropic Distillation Column (D-650)

Operation: Continuous

Design Description:

Orientation: Horizontal Bullet [U] Material of Construction: Carbon Steel
Dimensions: 10' 10" long, 4' 4" in diameter Volume: 79.2 ft^3 [22]
Support: Concrete Supports [37] Minimum Wall Thickness: 0.47 in [37]

Design Data: Hold Up Time: 5 min
Operating Pressure: 34 psi Design Pressure: 69 psi [36]
Operating Temperature: 120 °F Design Temperature: 170 °F [36]

Utilities: None Required
Controls: Automatic

Comments: See Section 600 in process flowsheet and Appendix F
Bare Module Cost: $42,000

TANK

Identification: Item: *Crotonate Removal Column Reflux Tank* Date: *April 13, 1999*
Item No.: *T-755*
No. Required: *1* By: *ABM*

Function: Stores condensed vapor from Crotonate Removal column (D-750)

Operation: Continuous

Design Description:

Orientation: Horizontal Bullet [U] Material of Construction: Carbon Steel
Support: Concrete Foundations [37] Volume: 305 ft^3 [22]
Dimensions: 15' 2" long, 5' 1" in diameter
Minimum Wall Thickness: 0.53 in [37]

Design Data: Hold Up Time: 5 min
Operating Pressure: 14.7 psi Design Pressure: 49.7 psi [36]
Operating Temperature: 212 °F Design Temperature: 262 °F [36]

Utilities: None Required
Controls: Automatic

Comments: See Section 700 in process flowsheet and Appendix F
Bare Module Cost: $68,000 [3]

TANK

Identification: Item: *Methyl Methacrylate Storage Tank* Date: *April 13, 1999*
Item No.: *T-790*
No. Required: *1* By: *ABM*

Function: Stores Final MMA Product

Operation: Continuous

Design Description:

Orientation: Vertical Cone Roof [U] Material of Construction: Carbon Steel
Dimensions: 125' 4" high, 41' 9" in diameter Volume: 172 M ft^3 [22]
Support: Concrete Foundations [37]
Minimum Wall Thickness: 0.53 in [37]

Design Data: Hold Up Time: 30 days
Operating Temperature: 77 °F Design Temperature : 127 °F [36]
Operating Pressure: 14.7 psi Design Pressure : 49.7 psi [36]

Utilities: None Required
Controls: Automatic

Comments: See Section 700 in process flowsheet and Appendix F
Bare Module Cost: $194,000 [3]

TANK

Identification: Item: *Inhibitor Storage Tank* Date: *April 13, 1999*
Item No.: *T-810*
No. Required: *1* By: *ABM*

Function: Stores 4-Methoxyphenol Inhibitor

Operation: Continuous

Design Description:

Orientation: Vertical Hopper Bin [U] Material of Construction: Carbon Steel
Dimensions: 5' 8" high, 1' 11" in diameter Volume: 16 ft^3 [22]
Support: Legs [37]
Minimum Wall Thickness: 0.40 in [37]

Design Data: Hold Up Time: 30 days
Operating Temperature: 77 °F Design Temperature : 127 °F [36]
Operating Pressure: 14.7 psi Design Pressure : 49.7 psi [36]

Utilities: None Required
Controls: Automatic

Comments: See Section 800 in process flowsheet and Appendix F
Bare Module Cost: $2,000 [3]

ALLOCATED UTILITY

Identification: Item: *Steam Furnace* Date: *April 13, 1999*
Item No.: *U-910*
No. Required: *1* By: *ABM*

Function: Provides Steam at 175 psi to other process units in the plant

Operation: Continuous

Design Description: Steam Furnace based on existing on-site design

Design Data: Upgrade in Steam Production: 32,400 lb/hr [all from 32]

9,500 lb/hr provided to Extractive Distillation Reboiler K-270
10,300 lb/hr provided to Azeotropic Distillation Reboiler K-670
7,200 lb/hr provided to Crotonate Removal Distillation Reboiler K-770
5,400 lb/hr provided to Catalyst Removal Flash Tank T-550

Utilities: None required
Controls: Automatic

Comments: See Section 900 in process flowsheet
Bare Module Cost: $1.62 MM [16a]

ALLOCATED UTILITY

Identification: Item: *Cooling Tower* Date: *April 13, 1999*
Item No.: *U-920*
No. Required: *1* By: *ABM*

Function: Provides Cooling Water at 90 °F to other process units in the plant

Operation: Continuous

Design Description: Cooling Tower based on existing on-site design

Design Data: Upgrade in Cooling Water Production: 3,570 gpm [all from 32]

526 gpm provided to Extractive Distillation Condenser C-260
1,390 gpm provided to Azeotropic Distillation Condenser C-660
632 gpm provided to Crotonate Removal Condenser C-760
166 gpm provided to Pre-Reaction Heat Exchanger H-410
837 gpm provided to Reactor Heat Exchanger H-460
13 gpm provided to Refrigerator U-930

Utilities: None required
Controls: Automatic

Comments: See Section 900 in process flowsheet
Bare Module Cost: $206 M [16a]

ALLOCATED UTILITY

Identification:
Item: *Refrigerator*
Item No.: *U-930*
No. Required: *1*
Date: *April 13, 1999*
By: *ABM*

Function: Provides Chilled Water to other process units in the plant

Operation: Continuous

Design Description: Refrigerator based on existing on-site design

Design Data:
Upgrade in Chilled Water Production: 11.6 tons
11.6 tons provided to Isomerization Reactor R-150 [32]

Utilities: None required
Controls: Automatic

Comments: See Section 900 in process flowsheet
Bare Module Cost: $16.0 M [16a]

ALLOCATED UTILITY

Identification: Item: *Incinerator* Date: *April 13, 1999*
Item No.: *None (Outside Battery Limit)*
No. Required: *1* By: *ABM*

Function: Disposes of unwanted byproducts and incompressible vapors

Operation: Continuous

Design Description: Incinerator based on off-site design

Design Data: Compensation for Incineration of material: 1.21 M lb/hr
12.1 M lb/hr provided to Incinerator [32]

Utilities: None required
Controls: Automatic

Comments: See Section 900 in process flowsheet
Bare Module Cost: S1 MM annually (assumed)

VALVE

Identification: Item: *Pressure Reduction Valve* Date: *April 13, 1999*
Item No.: *V-495 et al.*
No. Required: *1* By: *ABM*

Function: Reduces Pressure of stream (490)

Operation: Continuous

Design Description:
Type: Gate
Fail: Wide-Open

Design Data:

Inlet Pressure:	870.2	Inlet Temperature:	194	
Outlet Pressure:	16.8	Outlet Temperature:	141	

[all from 32]

Utilities: None required
Controls: Manual
Comments: See Section 400 in process flowsheet
Purchase Cost Range: $50-$150 (assumed)

Note: Instrumentation and piping costs are included in bare module cost estimations.
Detailed valve design is not in the scope of this report.
For information about the function of other valves in this process, see the piping and instrumentation diagram.

CONTROLLER

Identification: Item: *Valve 110 Controller* Date: *April 13, 1999*
Item No.: *Z-110 et al.*
No. Required: *3* By: *ABM*

Function: Maintains the pressure of stream 150 at a value of 327 psi.

Operation: Continuous

Design Description: Type: PID
Manipulated Variable: Flowrate
Controlled Variable: Pressure
Setpoint: 327 psi

Design Data: See Appendix L

Utilities: None required
Controls: Electronic

Comments: See piping and instrumentation diagram
Purchase Cost Range: $100-$2000

Note: Instrumentation and piping costs are included in bare module cost estimations.
Detailed controller design is not in the scope of this report.
For information about the function of other contollers in this process. see the piping and instrumentation diagram.

The overall control structure was based on Luyben's lecture notes. [39]

VIII. EQUIPMENT COST SUMMARY

No.	ID	Name	MOC	Bare Module Cost	Qty.	Total Bare Module Cost	% of Total Cost	Source
1	A-350	Catalyst Mixer Agitator	HC	$1,500	1	$1,500	0.01%	A
2	A-450	Reactor Agitator	HC	$1,500	1	$1,500	0.01%	A
3	A-810	Inhibitor Agitator	CS	$150	1	$150	<0.01%	A
4	B-590	Catalyst Azeotropic Blower	CS	$229,000	2	$458,000	4.35%	U
5	C-260	Extract Condenser	CS	$47,000	1	$47,000	0.45%	U
6	C-660	Azeotropic Condenser	CS	$77,000	1	$77,000	0.73%	U
7	C-760	Crotonate Removal Condenser	CS	$148,000	1	$148,000	1.41%	U
8	D-250/1	Extract Column	CS	$555,000	1	$555,000	5.27%	U
9	D-650	Azeotropic Column	CS	$167,000	1	$167,000	1.59%	U
10	D-750	Crotonate Removal Column	SSL	$947,000	1	$947,000	9.00%	U
11	H-410	Reactor Feed Heat Exchanger	CS	$18,000	1	$18,000	0.17%	U
12	H-460	Reactor Heat Exchanger	CS/HC	$190,000	1	$190,000	1.80%	U
13	K-270	Extract Reboiler	CS	$77,000	1	$77,000	0.73%	U
14	K-670	Azeotropic Reboiler	CS	$80,000	1	$80,000	0.76%	U
15	K-770	Crotonate Removal Reboiler	SS	$98,000	1	$98,000	0.93%	U
16	M-350	Catalyst Mixer	HCL	$5,000	1	$5,000	0.05%	U
17	M-810	Inhibitor Mixer	CS	$2,000	1	$2,000	0.02%	U
18	P-110	C_3 Feed Pump	CS	$57,500	2	$115,000	1.09%	U
19	P-210	Methanol Feed Pump	CS	$8,000	2	$16,000	0.15%	U
20	P-230	Methanol Extract Pump	CS	$30,500	2	$61,000	0.58%	U
21	P-255	Extract Reflux Pump	CS	$8,000	2	$16,000	0.15%	U
22	P-270	Extract Bottoms Pump	CS	$98,000	2	$196,000	1.86%	U
23	P-280	Extract Distillate Pump	CS	$8,000	2	$16,000	0.15%	U
24	P-350	Catalyst Batch Pump	HC	$30,500	2	$61,000	0.58%	U
25	P-390	Catalyst Reactor Feed Pump	HC	$197,000	2	$394,000	3.74%	U
26	P-450	Reactor Reflux Pump	HC	$814,000	2	$1,628,000	15.46%	U
27	P-655	Azeotropic Reflux Pump	CS	$8,000	2	$16,000	0.15%	U
28	P-670	Azeotropic Bottoms Pump	CS	$10,500	2	$21,000	0.20%	U
29	P-680	Azeotropic Distillate Pump	CS	$8,000	2	$16,000	0.15%	U
30	P-755	Crotonate Removal Reflux Pump	CS	$8,000	2	$16,000	0.15%	U
31	P-770	Crotonate Removal Bottoms Pump	CS	$8,000	2	$16,000	0.15%	U
32	P-780	Crotonate Removal Distillate Pump	CS	$8,000	2	$16,000	0.15%	U
33	P-810A	Inhibitor Crotonate Pump	CS	$8,000	2	$16,000	0.15%	U
34	P-810B	Inhibitor Azeotropic Pump	CS	$8,000	2	$16,000	0.15%	U
35	P-810C	Inhibitor Reactor Pump	CS	$8,000	2	$16,000	0.15%	U
36	R-150	Isomerization Chamber	CS	$84,000	2	$168,000	1.60%	U
37	R-450	Reactor	HC	$1,010,000	1	$1,010,000	9.59%	U

38	S-450	Reactor Spray	HC	$750	1	$750	0.01%	A
39	S-655	Azeotropic Spray	CS	$75	1	$75	0.00%	A
40	S-755	Crotonate Removal Spray	CS	$75	1	$75	0.00%	A
41	T-110	C3 Storage Tank	CS	$240,000	1	$240,000	2.78%	U
42	T-210	Methanol Storage Tank	CS	$39,000	1	$39,000	0.45%	U
43	T-255	Extract Reflux Drum	CS	$89,000	1	$89,000	1.03%	U
44	T-295	C3 By-Product Storage Tank	CS	$174,000	1	$174,000	2.02%	U
45	T-310	Palladium Ac Storage Tank	CS	$2,000	1	$2,000	0.02%	U
46	T-320	Phosphine Storage Tank	CS	$10,000	1	$10,000	0.12%	U
47	T-330	MSA Storage Tank	GL	$13,000	1	$13,000	0.15%	U
48	T-395	Catalyst Waste Storage Tank	HC	$5,000	1	$5,000	0.06%	U
49	T-550	Catalyst Flash Column	HCL	$103,000	1	$103,000	1.19%	U
50	T-655	Azeotropic Reflux Drum	CS	$42,000	1	$42,000	0.49%	U
51	T-755	Crotonate Removal Reflux Drum	CS	$68,000	1	$68,000	0.79%	U
52	T-790	MMA Storage Tank	CS	$194,000	1	$194,000	2.25%	U
53	T-810	Inhibitor Storage Tank	CS	$2,000	1	$2,000	0.02%	U
54	U-910	Steam Furnace	CS	$1,620,100	1	$1,621,000	18.77%	SSL
55	U-920	Cooling Tower	CS	$205,821	1	$206,000	2.39%	SSL
56	U-930	Refrigerator	CS	$15,162	1	$16,000	0.19%	SSL
57	None	Incinerator		$1,000,000	1	$1,000,000	9.85%	A
58	V-495	Valve 495	HC		1	$0	0.00%	-
59	Z-798	Controller 798	EL	$1,000	1	$1,000	0.01%	A
				Totals:		$10,149,000	100%	

iD numbers

A - Agitator
B - Blower
C - Condenser
D - Distillation Column
H - Heat Exchanger
K - Kettle Reboiler
M - Mixer
P – Pump
R – Reactor
S – Spray Nozzles
T – Tank
U – Allocated Utility
V – Valve
Z- Controller

MOC

CS - Carbon Steel
GL - Glass Lined
HC - Hastelloy-C
HCL - Hastelloy-C Lined
EL - Electronics
SS - Stainless Steel
SSL - Stainless Steel Lined

Source Legend:

U - Ulrich
Q - Quote
A - assumed

Equipment Type	% of Total Cost
Columns	15.86%
Heat Exchange Equipment	6.98%
Reactors	11.19%
Pumps and Blower	29.53%
Storage Tanks and Vessels	8.34%
Flash Column	0.98%
Allocated Utilites	27.01%
Other	0.10%
Total CBM of Equipment (1999)	**$10,525,050**
	100.00%

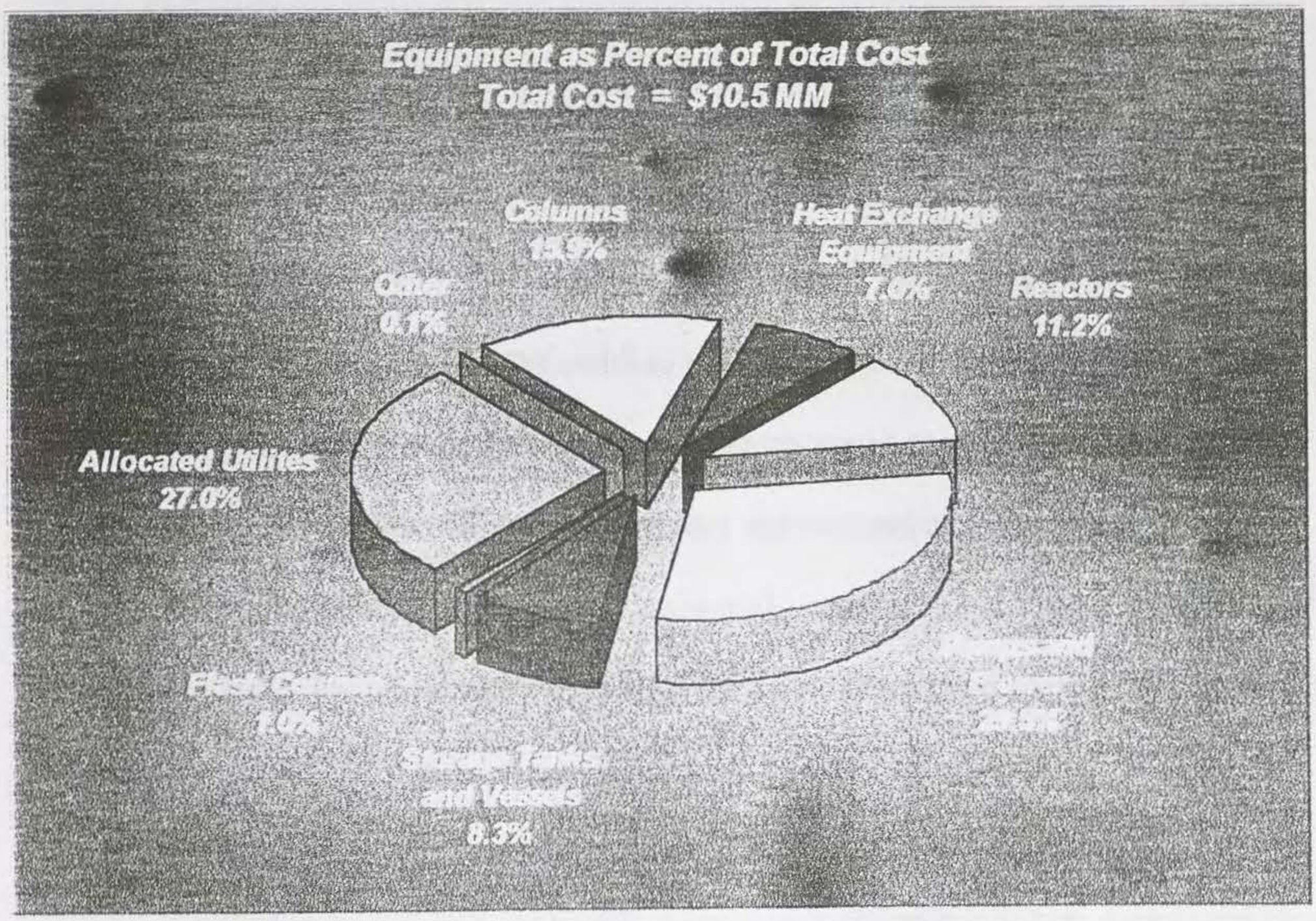


Figure 7: A breakdown of the equipment costs by equipment type.

IX. FIXED CAPITAL SUMMARY

The total fixed capital cost required for the initial construction of the plant is estimated to be $4.49 MM. This calculation was carried out on the previously mentioned Economics Spreadsheet on Microsoft Excel® Visual Basic Programming developed by Holger Nickisch, in the department of Chemical Engineering, University of Pennsylvania. The spreadsheet is attached in section XI Economic Analysis (p. 126).

This section involves the cost of capital process equipment. All units in the process flow sheet have been sized and priced according to Cost Charts of Ulrich referenced in *Process Design Principles*. Further references to the charts are made for each unit in the Equations and Nomenclature section. These calculations were carried out in an Excel® spreadsheet and functions such as the solver and goal seek were used to calculate any values requiring iterative procedures. The sheet was used in conjunction to the Cost Charts to generate bare module equipment costs. The distillation columns were oversized by 10% as a safety factor. Two of each piece of equipment that involved rotating parts such as pumps and blowers were purchased and installed. This would prevent plant shutdown in the event of mechanical failure. When it is necessary, the flow would be routed through the spare. The percentage of direct permanent investment for contingencies was set at 50%. This figure is usually 15% for most plants but since the chemistry of this process is fairly new and requires further study, and adding to this that this plant is only in its preliminary design phase, 50% seems to be a more realistic figure. No percentage of Total Depreciable Capital (C_{TDC}) was allocated to royalties, as this company is assumed to be a subsidiary of the Shell Oil Company. A figure of approximately $3.06 MM was devoted to Allocated Costs for Utilities and Related

Facilities as this plant is assumed to have its own Steam Furnace, Cooling Tower, Refrigeration unit for chilled water, and cost for dry land fill. The respective costs are $1.621 MM, $206,000, $16,000 and $1000. After these costs are converted to 1999 price [31], the figure of $3.06 MM results. This cost accounts for 20% of total purchased cost. The usual 10% were allocated to site preparation as well as start-up costs. There is no price advantage for the location of the U.S. Gulf Coast; hence the site factor is 1. These values, as well as the utility and miscellaneous costs, are referenced in Seider, Seader and Lewin. These costs are also summarized in the input sheet of the Excel® economic analysis spreadsheet, which include costs for maintenance, control room and utility lines (p. 139).

Storage tanks for all entering and leaving chemicals have been provided and are summarized by cost on the equipment list, and storage duration is mentioned in Appendix F. The chemicals are stored based on availability and importance in the process, i.e., feed reactants and end products would have a large storage supply. Most of the storage tanks are designed to hold material for 30 days with the exception of the C_3-byproduct, which is stored for one day, and the methanol storage, which is stored for 7 days.

Fixed Operating Costs

Methyl Methacrylate via Carboxymethylation

US Gulf Coast
100,000,000 lb per year
1999

				TOTAL
Operations				
Wages and Benefits	$	750,000		
Direct Salaries and Benefits	$	112,500		
Operating Supplies and Services	$	45,000		
Technical Assistance to Manuf.	$	55,000		
Control Laboratory	$	60,000		
Total Operations	$	1,023,000	$	1,023,000
Maintenance				
Wages and Benefits	$	568,855		
Salaries and Benefits	$	142,214		
Materials and Services	$	568,855		
Maintenance Overhead	$	28,443		
Total Maintenance	$	1,308,000	$	2,331,000
Operating Overhead				
General Plant Overhead	$	111,723		
Mechanical Department Services	$	37,766		
Employee Relations Department	$	92,841		
Business Services	$	116,444		
Total Operating Overhead	$	359,000	$	2,690,000
Property Taxes and Insurance	$	244,000	$	2,934,000
Replacement Catalyst	$	-	$	2,934,000
Total Fixed Costs (for Cash Flow Calculations):			**$**	**2,934,000**
Depreciation				
Direct Plant	$	1,300,000		
Allocated Plant	$	184,000		
Total Depreciation	$	1,484,000	$	4,418,000
Total Fixed Costs (for ROI Calculations):			**$**	**4,418,000**

X. CONSIDERATIONS

A. Environmental Considerations

This plant design has taken into account all necessary environmental concerns for the safety and well being of plant personnel and neighboring plant sites. The overall pressure of the plant equipment is above atmospheric pressure, which prevents any air leakage or oxygen entering the system. This is necessary because the reactant materials involved in the production of methyl methacrylate are corrosive and flammable. The concentrations of MA and PD, the most flammable components, are maintained below 50% to reduce the overall flammability. Carbon monoxide is a harmful reactant, and is in excess. The unreacted carbon monoxide exits the system as an incondensible vapor from the vents of the distillation reflux accumulators. This vent as well as other waste vents and unwanted by-products like methyl crotonate are piped to an incineration unit which disposes of the material appropriately. Due to the corrosive nature of the carboxymethylation catalyst the necessary pieces of equipment in the process have been lined with Hastelloy-C to prevent corrosion of unit material.

B. Catalyst Replacement

The potassium carbonate catalyst for the isomerization chamber (R-150) has to be replaced once in six months. A simple feasibility analysis was performed to conclude that it would be more cost effective to initially purchase two reactors to avoid plant shutdown for catalyst replacement. The spare catalyst would be stored in the spare isomerization unit and when the six-month time period expired, the control mechanism would transfer operation to the spare unit. The degraded potassium carbonate would be sent to a landfill. Regeneration or recovery of the consumed catalyst should be

investigated, but for the purpose of this design project and lack of further knowledge, it is assumed the catalyst is sent to a landfill.

The carboxymethylation catalyst is replaced one a month. Due to the value of palladium, the degraded catalyst would be sent back to the catalyst suppliers at no cost. The palladium suppliers would recover the palladium and dispose of the waste themselves. A control mechanism would simultaneously drain the degraded catalyst and introduce the fresh catalyst into the process once every month.

C. Safety Considerations

Methanesulfonic acid and carbon monoxide, require special safety considerations. Methanesulfonic acid is a toxic substance if inhaled or ingested. When handling this material, protective clothing must be worn. Masks should be worn when handling open vessels of MSA. Water showers will have to be included in strategic locations as a safety measure. If the material is absorbed through the skin or ingested in any way, it can destroy tissue and mucous membranes and the upper respiratory tract. If skin or eyes are exposed to MSA, immediate intensive flushing with water is required. The MSA storage tank (T-330) will have to be well sealed in order to prevent fumes from escaping.

Carbon monoxide is a toxic substance if inhaled. Masks will be stored in case of accidental release of carbon monoxide. No carbon monoxide is stored on the plant site at any time, which limits the possible danger of accidental release. Carbon monoxide enters the plant battery limits through a pipeline and leaves in the vent streams. The off site incineration unit will have to ensure that all waste effluents comply with the corresponding Environmental Protection Agency requirements.

Methyl Acetylene and propadiene are highly flammable components in the C_3 feed stream. MA and PD are diluted in propane and propylene to reduce the flammability of this stream. Throughout the plant the concentration of MA and PD is kept below 50% to reduce the risk of fires. The plant will be designed to contain fires or explosions in the unlikely event of an accident.

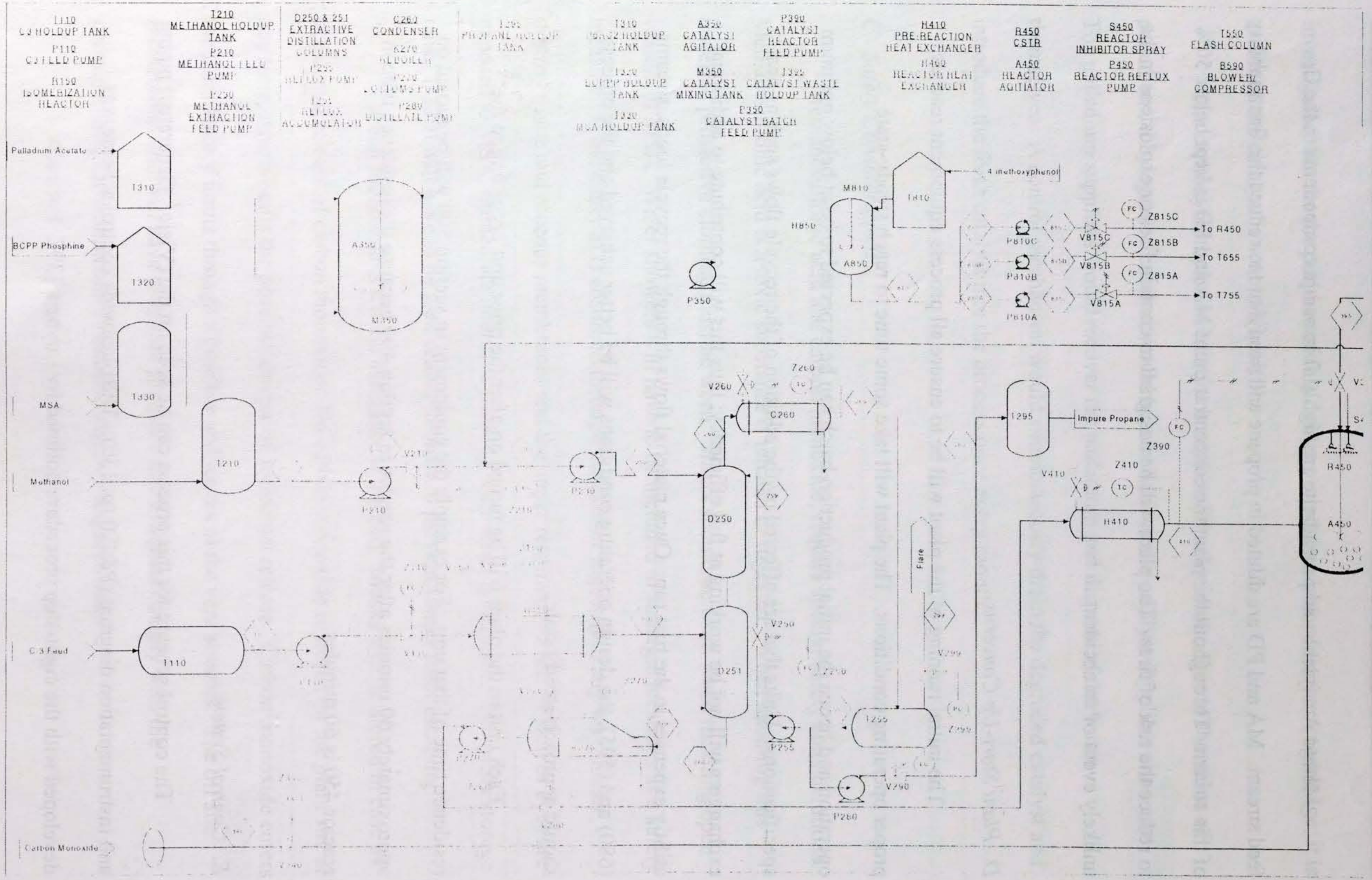
D. Plant Start-Up Concerns

The initial running of the plant will be to ensure all process equipment reaches proper operating conditions. The plant will take some time to reach steady-state operation and hence the initial production batch can be expected to be at below optimum specifications. Units that are affected by the addition of the recycle flows such as heat exchangers will not be working at full efficiency; thus this will contribute to additional utilitiy expenses in the first run. Once material flows through the recycle loops, streams (680) and (595), the design operating conditions will be better achieved and the process should approach steady state.

Each unit in the plant will be turned on after the prior unit according to the residence time of that unit. For example the equipment in section 500 will be turned on approximately 60 minutes after the reactor in section 400 because the residence time in reactor 450 is 60 minutes.

E. Control System

The control scheme for this process can be seen on the (Visio® Generated) piping and instrumentation diagram (P&ID) (p. 130). The plantwide control scheme was developed with the eight-step procedure outlined by Luyben. [39]. For each


T110
C3 HOLDUP TANK
P110
C3 FEED PUMP
R150
ISOMERIZATION REACTOR
T210
METHANOL HOLDUP TANK
P210
METHANOL FEED PUMP
P230
METHANOL EXTRACTION FEED PUMP
D250 & 251
EXTRACTIVE DISTILLATION COLUMNS
P255
REFLUX PUMP
T255
REFLUX ACCUMULATOR
C260
CONDENSER
R270
REBOILER
P270
COLUMN PUMP
P280
DISTILLATE PUMP
T295
PROPANE HOLDUP TANK
T310
CATALYST HOLDUP TANK
T320
BCPP HOLDUP TANK
T330
MSA HOLDUP TANK
A350
CATALYST AGITATOR
M350
CATALYST MIXING TANK
P350
CATALYST BATCH FEED PUMP
P390
CATALYST REACTOR FEED PUMP
T395
CATALYST WASTE HOLDUP TANK
H410
PRE-REACTION HEAT EXCHANGER
H400
REACTOR HEAT EXCHANGER
R450
CSTR
A450
REACTOR AGITATOR
S450
REACTOR INHIBITOR SPRAY
P450
REACTOR REFLUX PUMP
T550
FLASH COLUMN
B590
BLOWER/ COMPRESSOR
Palladium Acetate
BCPP Phosphine
MSA
Methanol
C-3 Feed
Carbon Monoxide
4 methoxyphenol
Impure Propane
Flare
To R450
To T655
To T755
Z815C
Z815B
Z815A
Z260
Z390
Z410
Z299
V815C
V815B
V815A
V260
V290
V410
P810C
P810B
P810A
M810
H850
A850
P350
P210
P230
P240
P255
P280
P410
R450
A450
H410
T110
T210
T255
T295
T310
T320
T330
T395
D250
D251
C260

D650 AZEOTROPIC DISTILLATION COLUMN

S655 REFLUX INHIBITOR SPRAY

C660 CONDENSER

K670 REBOILER

I655 REFLUX ACCUMULATOR

P655 REFLUX PUMP

P660 DISTILLATE PUMP

D750 CRUDE MMA REMOVAL DISTILLATION COLUMN

I755 REFLUX ACCUMULATOR

S755 REFLUX INHIBITOR SPRAY

P755 REFLUX PUMP

C760 CONDENSER

K770 REBOILER

P770 BOTTOMS PUMP

P780 DISTILLATE PUMP

T790 PRODUCT HOLDUP TANK

T810 INHIBITOR HOLDUP TANK

M810 INHIBITOR MIXING TANK

A850 INHIBITOR AGITATOR

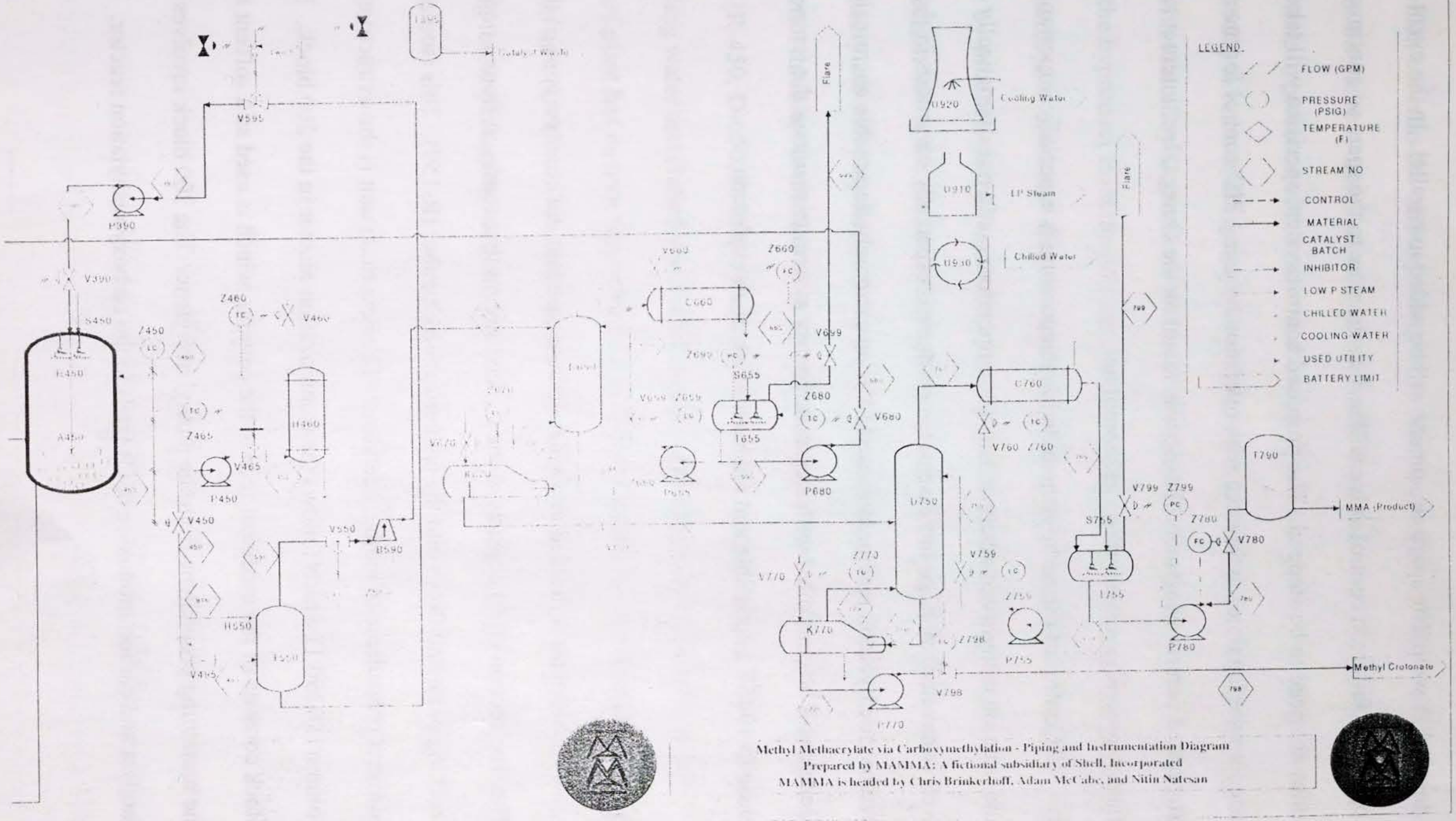
P810A, B, C INHIBITOR FEED PUMPS

H950 INHIBITOR HEATER

U910 STEAM FURNACE

U920 COOLING TOWER

U930 REFRIGERATOR



Methyl Methacrylate via Carboxymethylation - Piping and Instrumentation Diagram
Prepared by MAMMA: A fictional subsidiary of Shell, Incorporated
MAMMA is headed by Chris Brinkerhoff, Adam McCabe, and Nitin Natesan

piece of equipment that contains a spare, the corresponding control valves have to be doubled as well. The spare equipment will be added in parallel. In the event of an operation failure, a control valve will switch the flow to the spare so continuous operation does not need to be stopped. The proposed control system specified will take into account the lag times associated with operation by using PID control for many units. The suggested control equipment for use was found on the Omega, Inc. internet site (http://www.omega.com), and is Y2K compliant.

Control of the carboxymethylation temperature is especially important, because the reaction is highly exothermic and the temperature could rise dramatically if it is not well controlled. A large increase in temperature is especially hazardous in the carboxymethylation reactor because MA is an extremely flammable chemical. The reactor will be controlled with a cascade control system to maintain the temperature as close to 194 ^{o}F as possible and reduce the risk of an explosion.

G. Plant Layout

This plant is divided into nine sections based on the main purpose of that section. The first section (100) consists of the C_3 feed stream that comes in from a naphtha cracking plant and flows into the isomerization chamber (R-150). This isomerization converts propadiene to methyl acetylene. The next main unit is the extractive distillation column (D-250/1) which follows the isomerization reactor in the 200 block. The 200 block consists of the methanol feed to the column, which is used as a solvent to extract the remaining propadiene from the methyl acetylene. The 300 block involves only the catalyst and carbon monoxide (CO) feeds to the carboxymethylation reactor. This block

prepares the catalyst and the CO for the reactor. The central section to the process is the 400 block, which contains the carboxymethylation reactor (R-450). Methyl methacrylate is produced in the carboxymethylation reactor (R-450) by combining CO, methanol, and methyl acetylene in presence of the catalyst solution. The next section 500, consists of a flash unit (T-550) to remove the corrosive catalyst so that downstream units do not need to be lined with Hastelloy-C. Sections 600 and 700 are distillation units that separate the solvent and the byproduct from the product. The azeotropic distillation column (D-650) separates and recycles methanol from the methyl methacrylate. The 700 column (D-770) removes the by-product, methyl crotonate, which is sent to an incineration unit for disposal. Section 800 is the inhibitor distribution section. If an inhibitor is not used methyl methacrylate will polymerize into poly-methyl methacrylate. The 4-methoxyphenol inhibitor is distributed to the reflux accumulator of all major columns and the reactor (R-450, D-650, D-750). The last section, 900, consists of the main utilities. Steam, cooling water and chilled water are brought to the necessary conditions in this section. This plant has its own Steam Furnace (U-910), Cooling Tower (U-920) and a Refrigeration unit (U-930). The final product (99.9% MMA) is stored in a storage tank before going to the packaging section.

XI. ECONOMIC ANALYSIS

The product of interest in this process is methyl methacrylate. This product currently sells on the bulk product market at approximately 60 cents ($0.60) per pound of MMA. All of the raw materials used in the process have to be purchased at bulk market price. The cost of capital equipment and raw materials have been summarized in a Microsoft Excel® spreadsheet developed by Holger Nickisch (p. 135). The process also involves the production of two by-products: methyl crotonate and a light C-3 stream. It was discovered through preliminary market research, that the market for methyl crotonate is very small to non-existent therefore the methyl crotonate is sent to an incinerator for disposal. The raw material feed C_3 stream is bought for 6 cents ($0.06) per pound from a neighboring naphtha cracking plant and the byproduct light C_3 stream is sold back to the naphtha cracking plant as fuel at 4 cents ($0.04) per pound. The plant runs 7920 hours per year, and assuming that the plant operates at 90% of its capacity, it produces 100 MM lbs. of methyl methacrylate per year. At 60 cents per pound, the yearly gross product credit is thus $60 MM. Standard percentages for allocated costs were used according to *Process Design Principles*.

The carboxymethylation catalyst gradually loses activity and once a month the catalyst must be replaced to maintain the desired conversion. Activation of the degraded catalyst for reuse, would be an expensive and financially unfavorable procedure. The catalyst is returned to the supplier at no cost so that the suppliers can recover the palladium themselves. This method of recycling the used catalyst to the supplier was recommended by various meetings with industrial consultants, and it is also a common practice in industry. The three-part catalyst mixture costs $158,000 per batch. The potassium carbonate catalyst used in the isomerization chamber costs $11,500 per batch.

This catalyst is replaced every six months and a spare is stored in a second, unused isomerization reactor. Two isomerization units have been specified since the cost of shutting the plant down for a day to replace the potassium carbonate every six months outweighed the cost of purchasing another reactor. A one-day catalyst replacement procedure translates to a $182,000 (twice a year) loss in product revenue compared to a one-time isomerization vessel cost of $168,000.

All equipment costing has been done using either direct quotes from industrial consultants, manufacturers, estimations based on industry prices or through the Ulrich Cost Charts. Major equipment has been over estimated by rounding to the nearest thousand dollars. Sizing and costing summaries are provided in Appendix F.

In addition to major units, this plant is assumed to have its own steam furnace, cooling tower and refrigeration unit. These utilities have been factored into the cost as Allocated Utility and Related Facility Cost. Apart from basic percentages summarized in the Economics Spread Sheet (p. 139) taken from *Process Design Principles*, the plant assumes 3 operators per shifts, 5 shifts per day and $50,000 per operator as annual wage. With all this inputted, total fixed costs are $4,490,000, total variable costs are $27,000,000 and this results in an investor's rate of return (IRR) of 39.5%. A sensitivity analysis has been done on the effect of price of raw materials and product on the IRR. This analysis is useful in evaluating the long term profitability of the plant and accounting for the uncertainty of future raw material prices.

As would be expected, an increase in product price would drive the IRR up and likewise, a decrease in raw materials and catalyst price would do the same. A sensitivity analysis was completed on the price variation of the most price sensitive catalyst part –

palladium acetate, all three primary reactants (MA, CO, and Methanol), and the MMA product.

The IRR is most sensitive to the selling price of MMA. The current market price of MMA is 60 cents per pound, and the analysis shown on the chart below (see Appendix I) indicates that the IRR will drop below 20% if the MMA price drops below 37 cents per pound. The annual inflation rate was assumed to be 1.5%. The price of product at the current inflation rate would climb to 75 cents per pound at the end of 15 years (plant life). The only reason that the price of MMA would plummet would be because of a decline in demand or a sharp increase in MMA production. These are both unlikely occurrences as the market outlook mentioned in the introduction indicates strong growth. Adding to this, the price of MMA would have to drop 60% before the continuity of production became a chief concern. In terms of reactant and palladium acetate catalyst prices, the current market prices compared with prices at which IRR is 20% are summarized below:

	Current Market Price	Price at which IRR = 20%	%Price Increase
Methanol	$0.40 /lb	$1.62 /lb	405
Carbon Monoxide	$0.12 /lb	$0.69 /lb	575
Methyl Acetyiene	$0.06 /lb	$0.26 /lb	433
Palladium Acetate	$30000 /batch	≅ $2,000,000 /batch	6600
Methyl Methacrylate	$0.60 /lb	$0.37 /lb	-162

As can be seen, the price of the three raw material reactants would have to increase by an average of 400% for the IRR to drop below 20%. Thus variation in prices would have to be of large magnitude to affect IRR and profitability of running the plant, except for palladium acetate. The batch price of palladium acetate would have to increase 66 times its current market price for the IRR to drop below 20%. In addition to this a worst- case scenario was investigated where the reactant prices all increased by a percentage while

simultaneously, the product price dropped by the same percentage. At a 20% reactant price increase, and reduction of product price, the IRR is 20%. From the sensitivity analysis, we can conclude that the IRR is fairly resistant to reactant, product and catalyst price changes. The price of palladium has fluctuated intensely over the last 15 years and a current industry quote prices it at $7.50 per gram. The fluctuation over time can be seen in a graph of historical data (Appendix I).

The optimization to minimize cost based on process design was also carried out. The azeotropic distillation column was optimized based on number of trays, amount recycled, and utilities used to produce the minimum cost of the unit. Similarly, the extraction unit was optimized based on amount of methanol, number of trays and utilities. Lastly, the crotonate removal column is optimized based on number of trays and utilities.

Optimizing these properties of each column in this way resulted in the smallest column possible that achieved the necessary separation. The way in which the optimization was carried out was with the use of ASPEN® simulation software. The main principle behind the optimization was to minimize the size of the column by modifying the other variables like reflux ratio and amount recycled. ASPEN® would then calculate the new design and then a rough cost comparison would be done with the "six-tenths rule." In addition to the unit optimization, older process designs were evaluated in terms of cost benefit. Previous designs included:

Scenario	Equipment	Total Cost
1	One Flash	**$5,529,000**
2	Two Flashes	**$6,142,000**
3	Column with no Condenser	**$6,651,000**

The optimization revealed scenario (1) as the most economical design (Appendix H).

After the optimization, sensitivity analysis and over estimation of equipment costs the IRR of 39.5% remains standing. The cash flows sheet is shown on page 144. The calculated IRR for this plant makes this design a very attractive process to investigate further.

INPUT FORM

PROCESS:		Methyl Methacrylate via Carboxymethylation					
PRODUCT:		Methyl Methacrylate			OPERATING HOURS PER YEAR	7920	
CAPACITY:	100,000,000	PER YEAR ☑	12,626	PER HOUR ☐	UNITS:	lb	
THIS YEAR:		1999	MARKET PRICE OF PRODUCT ($):		0.60		
DAYS OF PRODUCT INVENTORY:		30	LOCATION:		US Gulf Coast		

INPUT FOR VENTURE GUIDANCE APPRAISAL (check box to hide classification calculation) ☑

PURCHASED COST OF EQUIPMENT (Engineered)

Equipment Type 1		Cost in $	
Equipment Type 2		Cost in $	
Equipment Type 3		Cost in $	
Equipment Type 4		Cost in $	
Equipment Type 5		Cost in $	
Equipment Type 6		Cost in $	
Equipment Type 7		Cost in $	
Equipment Type 8		Cost in $	
Equipment Type 9		Cost in $	
Equipment Type 10		Cost in $	

Percentage of Purchased Costs for Installation Materials:		%
Percentage of Purchased Costs for Labor :		%
Indirect Project Expenses		
Percentage of Purchased Costs for Freight, Insurance and Taxes :		%
Percentage of Purchased Costs for Construction Overhead:		%
Percentage of Purchased Costs for Contractor Engineering Expenses:		%

Equipment Type 1	Reactor and associated heat exchanger	Cost in $	1,199,000	Bare Module Factor	1
Equipment Type 2	Blower	Cost in $	229,000	Bare Module Factor	1
Equipment Type 3	Flash vessel	Cost in $	103,000	Bare Module Factor	1
Equipment Type 4	Pumps	Cost in $	2,642,000	Bare Module Factor	1
Equipment Type 5	Columns (including reflux tank, reboiler & condens	Cost in $	2,012,000	Bare Module Factor	1
Equipment Type 6	Heat exchanger	Cost in $	18,000	Bare Module Factor	1
Equipment Type 7	Isomerization reactor	Cost in $	168,000	Bare Module Factor	1
Equipment Type 8	Storage Vessels	Cost in $	682,000	Bare Module Factor	1
Equipment Type 9	Other (Sprays, Mixers, Agitators)	Cost in $	12,000	Bare Module Factor	1
Equipment Type 10		Cost in $		Bare Module Factor	

Total Capital Investment (see Table 9.2)

Percentage of Total Bare Module Costs for Site Preparation and Service Facilities:	10.00	%	
Allocated Utility and Related Facility Costs (see Table 9.4):	3,063,000.00	$	
Percentage of Direct Permanent Investment for Contingencies:	50.00	%	
Land: Enter either a dollar value or a percentage of Total Depreciable Capital:		$ or	2 % of TDC
Percentage of Total Depreciable Capital for Royalties:	-	%	
Percentage of Total Depreciable Capital for Start-Up:	10.00	%	
Site Factor (see Table 9.5)	1.00		

Working Capital

Inventories of Reactants are entered below in the section for Variable Costs. If you want to include reactant inventory in your Working Capital Calculations, please enter the data below first. Enter the reactant, and all other relevant data (lines 57 and beyond)

Other Items for Working Capital				Days of Accts Rec.
Item 1	Bis(3-chlorophenyl)(2-pyridyl)phosphine	Cost ($)	123,000.00	30
Item 2	Palladium Acetate	Cost ($)	30,000.00	
Item 3	Methanesulfonic Acid	Cost ($)	5,000.00	
Item 4	Potassium Carbonate on Alumina	Cost ($)	12,000.00	
Item 5		Cost ($)		
Item 6		Cost ($)		

INPUT FOR VARIABLE COST CALCULATIONS (see Table 10.1)

Reactants (check box on left if you intend to keep inventory of Reactant)

Reactant 1	Methanol	Units	gal	☑	How many days? 7
Reactant 2	Carbon Monoxide	Units	lb	☑	
Reactant 3	C-3 Stream	Units	lb	☑	How many days? 1
Reactant 4	4-Methoxyphenol	Units	kg	☑	How many days? 30
Reactant 5	Palladium Acetate	Units	batch	☑	How many days? 30
Reactant 6	Methanesulfonic Acid	Units	batch	☑	How many days? 30
Reactant 7	Bis(3-chlorophenyl)(2-pyridyl)phosphine	Units	batch	☑	How many days? 30
Reactant 8	Potassium Carbonate on Alumina	Units	batch	☑	How many days? 180
Reactant 9		Units		☐	
Reactant 10		Units		☐	
Reactant 11		Units		☐	
Reactant 12		Units		☐	
Reactant 13		Units		☐	
Reactant 14		Units		☐	

Enter Reactant Data | Reset Reactant Entry Form

Cost ($) per gal Methanol	2.4
gal Methanol per lb Methyl Methacrylate	0.003
Cost ($) per lb Carbon Monoxide	0.12
lb Carbon Monoxide per lb Methyl Methacrylate	1.0145
Cost ($) per lb C-3 Stream	0.25
lb C-3 Stream per lb Methyl Methacrylate	0.01
Cost ($) per kg 4-Methoxyphenol	20
kg 4-Methoxyphenol per lb Methyl Methacrylate	0.00087
Cost ($) per batch Palladium Acetate	30000
batch Palladium Acetate per lb Methyl Methacrylate	0.00000012
Cost ($) per batch Methanesulfonic Acid	5000
batch Methanesulfonic Acid per lb Methyl Methacrylate	0.00000012
Cost ($) per batch Bis(3-chlorophenyl)(2-pyridyl)phosphine	123000
batch Bis(3-chlorophenyl)(2-pyridyl)phosphine per lb Methyl Methacryl	0.000000012
Cost ($) per batch Potassium Carbonate on Alumina	12000
batch Potassium Carbonate on Alumina per lb Methyl Methacrylate	0.00000002

Utilities(enter the units then check the box)

HP Steam		☐			
LP Steam	1000 lbs	☑	Cost($) per 1000 lbs:	6.00	1000 lbs of LP Steam per lb of Methyl Methacrylate 0.00303
Process Water		☐			
Cooling Water	1000 gal	☑	Cost($) per 1000 gal:	0.05	1000 gal of Cooling Water per lb of Methyl Methacrylate 0.019
Natural Gas		☐			
Electricity	kWhr	☑	Cost($) per kWhr:	0.04	kWhr of Electricity per lb of Methyl Methacrylate 0.0159
Refrigeration	ton-day	☑	Cost($) per ton-day:	2.06	ton-day of Refrigeration per lb of Methyl Methacrylate 0.000038
Dry Landfill	lb	☑	Cost($) per lb:	0.0625	lb of Dry Landfill per lb of Methyl Methacrylate 0.00016
(name)		☐			

Other

1. | Unit Cost ($) | Units per lb Methyl Methacrylate

2:		Unit Cost ($)		Units per lb Methyl Methacrylate	
3:		Unit Cost ($)		Units per lb Methyl Methacrylate	
4:		Unit Cost ($)		Units per lb Methyl Methacrylate	

Selling/Transfer Expense	3	% of Sales
Direct Research	4.8	% of Sales
Allocated Research	0.5	% of Sales
Administrative Expense	2	% of Sales
Management Incentive Compensation:	1.25	% of Sales

Byproducts

If there are valueable byproducts, click here! ENTER BYPRODUCT DATA Total Byproduct Credit= 0.60 $ lb of Methyl Methacrylate

Packaging

Labor:	0.00001	$ per unit product
Materials:	0.000001	$ per unit product

INPUT FOR FIXED COST CALCULATIONS (see Table 10.1)

Operations

Number of Operators per Shift:	3	(assuming 5 Shifts)
Annual Wages per Operator:	50,000	$ Includes Benefits: ☑
Direct Salaries and Benefits	15	% of wages
Operating Supplies and Services:	6	% of wages
Technical Assistance to Manuf.:	55,000	in $/labor yr
Control Laboratory:	60,000	in $/labor yr

Maintenance

Wages:	3.5	% of Total Depreciable Capital Includes Benefits: ☑
Salaries and Benefits:	25	% of Maintenance Wages and Benefits
Materials and Services:	100	% of Maintenance Wages and Benefits
Maintenance Overhead:	5	% of Maintenance Wages and Benefits

Operating Overhead

General Plant Overhead:	7.1	% of Maintenance and Operations Salaries, Wages and Benefits
Mechanical Department Services:	2.4	% of Maintenance and Operations Salaries, Wages and Benefits
Employee Relations Department:	5.9	% of Maintenance and Operations Salaries, Wages and Benefits
Business Services:	7.4	% of Maintenance and Operations Salaries, Wages and Benefits

Property Taxes and Insurance

Property Taxes and Insurance	1.5	% of Total Depreciable Capital

Depreciation

Direct Plant	8	% of Total Depreciable Capital
Allocated Plant	6	% of Allocated Costs

Catalyst Replacement

Catalyst Replacement	0	$

INPUT FOR CASH FLOW ANALYSIS

Please click the enter button on the right after entering the data in the next two lines!

Design Phase	1	in yrs.
Construction Phase	2	in yrs.

Enter

By default, the Total Permanent Investment Costs are spread evenly over the design & construction phase. (Working Capital is always introduced in the last year of construction.) If you would like to change the default

Click Here !

Reset to Default !

Estimated Life	15	in yrs.
Cost of Capital	15	%
Inflation Rate	1.5	%
Income Tax Rate	37	%

Depreciation Schedule

Pick MARCS Tax-Basis Depreciation Schedule

5 year ☑ 7 year ☐ 10 year ☐ 15 year ☐

Venture Guidance Appraisal

Methyl Methacrylate via Carboxymethylation

US Gulf Coast
100,000,000 lb per year
1999

Individual Equipment Items					
Reactor and associated heat exchanger			$	1,199,000	
Blower			$	229,000	
Flash vessel			$	103,000	
Pumps			$	2,642,000	
Columns (including reflux tank, reboiler & col			$	2,012,000	
Heat exchanger			$	18,000	
Isomerization reactor			$	168,000	
Storage Vessels			$	682,000	
Other (Sprays, Mixers, Agitators)			$	12,000	
Total Bare Module Cost of Equipment					$ 7,065,000
Cost of Site Preparation and Service Facilities			$	707,000	
Alloc. Costs for Utilities and Related Facilities			$	3,063,000	
Direct Permanent Investment					$ 10,835,000
Cost of Contingencies			$	5,418,000	
Total Depreciable Capital					$ 16,253,000
Cost of Land			$	325,000	
Cost of Royalties			$	-	
Cost of Start-Up			$	1,625,000	
Total Permanent Investment					$ 18,203,000
Working Capital					
Inventory					
Methyl Methacrylate	9,090,909	lb	$	5,454,545	
Methanol	345,758	gal	$	138,303	
C-3 Stream	306,061	lb	$	18,364	
4-Methoxyphenol	609	kg	$	30	
Palladium Acetate	1	batch	$	32,727	
Methanesulfonic Acic	1	batch	$	5,455	
Bis(3-chlorophenyl)(2	1	batch	$	134,182	
Potassium Carbonate	1	batch	$	13,091	
Other					
Bis(3-chlorophenyl)(2-pyridyl)phosphine			$	123,000	
Palladium Acetate			$	30,000	
Methanesulfonic Acid			$	5,000	
Potassium Carbonate on Alumina			$	12,000	
Accounts Receivable					
30 days			$	5,454,545	
Total Working Capital				$ 11,421,000	
Total Capital Investment					$ 29,624,000

Total Permanent Investment / Total Purchase Cost of Equipment = 2.577

Variable Operating Costs

Methyl Methacrylate via Carboxymethylation

US Gulf Coast
100,000,000 lb per year
1999

Feed Stock				**TOTAL**
Methanol	6.52 ¢/lb of Methyl Meth			
Carbon Monoxide	4.18 ¢/lb of Methyl Meth			
C-3 Stream	6.06 ¢/lb of Methyl Meth			
4-Methoxyphenol	0.00 ¢/lb of Methyl Meth			
Palladium Acetate	0.36 ¢/lb of Methyl Meth			
Methanesulfonic Ac	0.06 ¢/lb of Methyl Meth			
Bis(3-chlorophenyl)	1.48 ¢/lb of Methyl Meth			
Potassium Carbona	0.02 ¢/lb of Methyl Meth			
Total Feed Stock:	**18.68** ¢/lb of Methyl Methac	→	**$ 18,676,000**	**$ 18,676,000**
Utilities				
LP Steam	1.82 ¢/lb of Methyl Meth			
Cooling Water	0.10 ¢/lb of Methyl Meth			
Electricity	0.07 ¢/lb of Methyl Meth			
Refrigeration	0.01 ¢/lb of Methyl Meth			
Dry Landfill	0.00 ¢/lb of Methyl Meth			
Total Utilities:	**1.99** ¢/lb of Methyl Methac	→	**$ 1,995,000**	**$ 20,671,000**
Other				
Total Other	**0.00** ¢ /lb of Methyl Methac	→	**$ -**	**$ 20,671,000**
Byproduct Credit	(0.60) ¢ /lb of Methyl Methac	→	**$ (602,000)**	**$ 20,069,000**
Packaging				
Labor	0.00 ¢ /lb of Methyl Meth			
Materials	0.00 ¢ /lb of Methyl Meth			
Total Packaging	**0.00** ¢ /lb of Methyl Methac	→	**$ 1,000.00**	**$ 20,070,000**
Selling/Transfer Expense	1.80 ¢ /lb of Methyl Methacrylate			
Direct Research	2.88 ¢ /lb of Methyl Methacrylate			
Allocated Research	0.30 ¢ /lb of Methyl Methacrylate			
Administrative Expense	1.20 ¢ /lb of Methyl Methacrylate			
Mgmt Incentive Compensation	0.75 ¢ /lb of Methyl Methacrylate			
Subtotal	**6.93** ¢ /lb of Methyl Methac	→	**$ 6,930,000**	**$ 27,000,000**
Total Variable Costs:	**27.00** ¢ /lb of Methyl Methac	→		**$ 27,000,000**

Fixed Operating Costs

Methyl Methacrylate via Carboxymethylation

US Gulf Coast
100,000,000 lb per year
1999

				TOTAL
Operations				
Wages and Benefits	$	750,000		
Direct Salaries and Benefits	$	112,500		
Operating Supplies and Services	$	45,000		
Technical Assistance to Manuf.	$	55,000		
Control Laboratory	$	60,000		
Total Operations	$	1,023,000	$	1,023,000
Maintenance				
Wages and Benefits	$	568,855		
Salaries and Benefits	$	142,214		
Materials and Services	$	568,855		
Maintenance Overhead	$	28,443		
Total Maintenance	$	1,308,000	$	2,331,000
Operating Overhead				
General Plant Overhead	$	111,723		
Mechanical Department Services	$	37,766		
Employee Relations Department	$	92,841		
Business Services	$	116,444		
Total Operating Overhead	$	359,000	$	2,690,000
Property Taxes and Insurance	$	244,000	$	2,934,000
Replacement Catalyst	$	-	$	2,934,000
Total Fixed Costs (for Cash Flow Calculations):			$	2,934,000
Depreciation				
Direct Plant	$	1,300,000		
Allocated Plant	$	184,000		
Total Depreciation	$	1,484,000	$	4,418,000
Total Fixed Costs (for ROI Calculations):			$	4,418,000

Cash Flows

Methyl Methacrylate via Carboxymethylation

US Gulf Coast

100,000,000 lb per year

	DESIGN	CONSTRUCTION	CONSTRUCTION	PRODUCTION	PRODUCTION	PRODUCTION	PRODUCTION	PRODUCTION
Year	1999	2000	2001	2002	2003	2004	2005	2006
% of Capacity	0	0	0	45	67.5	90	90	90
Sales				$ 28,233,000	$ 42,985,000	$ 58,173,000	$ 59,046,000	$ 59,932,000
Capital Cost	$ (6,068,000)	$ (6,159,000)	$ (6,251,000)					
Working Capital			$ (11,943,000)	$ (171,000)	$ (171,000)	$ (171,000)	$ (171,000)	$ (171,000)
Variable Cost				$ (12,705,000)	$ (19,343,000)	$ (26,178,000)	$ (26,571,000)	$ (26,969,000)
Fixed Cost				$ (3,068,000)	$ (3,114,000)	$ (3,161,000)	$ (3,208,000)	$ (3,256,000)
Depreciation				$ (3,696,000)	$ (5,913,000)	$ (3,548,000)	$ (2,129,000)	$ (2,129,000)
Taxable Income	$ (6,068,000)	$ (6,159,000)	$ (18,194,000)	$ 8,593,000	$ 14,444,000	$ 25,115,000	$ 26,967,000	$ 27,407,000
Income Tax				$ (3,179,000)	$ (5,344,000)	$ (9,293,000)	$ (9,978,000)	$ (10,141,000)
Net Earnings	$ (6,068,000)	$ (6,159,000)	$ (18,194,000)	$ 5,414,000	$ 9,100,000	$ 15,822,000	$ 16,989,000	$ 17,266,000
Annual Cash	$ (6,068,000)	$ (6,159,000)	$ (18,194,000)	$ 9,110,000	$ 15,013,000	$ 19,370,000	$ 19,118,000	$ 19,395,000
Cumulative PV @ 15%	$ (6,068,000)	$ (11,424,000)	$ (25,181,000)	$ (19,191,000)	$ (10,607,000)	$ (977,000)	$ 7,288,000	$ 14,579,000

ROI (Third Year of Production)		
Sales	$ 58,173,000	
Variable Costs	$ (26,178,000)	
Fixed Costs	$ (4,830,832)	
Gross Income	$ 27,164,000	
Income Tax	$ (10,051,000)	
Net Income	$17,113,000	56.25%

Capital Investment
$ 30,421,000

NPV
$ 53,112,000

IRR
39.98%

PRODUCTION 2007 90	PRODUCTION 2008 90	PRODUCTION 2009 90	PRODUCTION 2010 90	PRODUCTION 2011 90	PRODUCTION 2012 90	PRODUCTION 2013 90	PRODUCTION 2014 90	PRODUCTION 2015 90	PRODUCTION 2016 90
$ 60,831,000	$ 61,743,000	$ 62,669,000	$ 63,609,000	$ 64,563,000	$ 65,532,000	$ 66,515,000	$ 67,513,000	$ 68,525,000	$ 69,553,000
$ (171,000)	$ (171,000)	$ (171,000)	$ (171,000)	$ (171,000)	$ (171,000)	$ (171,000)	$ (171,000)	$ (171,000)	$ 14,931,000
$ (27,374,000)	$ (27,784,000)	$ (28,201,000)	$ (28,624,000)	$ (29,054,000)	$ (29,489,000)	$ (29,932,000)	$ (30,381,000)	$ (30,836,000)	$ (31,299,000)
$ (3,305,000)	$ (3,355,000)	$ (3,405,000)	$ (3,456,000)	$ (3,508,000)	$ (3,561,000)	$ (3,614,000)	$ (3,668,000)	$ (3,723,000)	$ (3,779,000)
$ (1,064,000)									
$ 28,917,000	$ 30,433,000	$ 30,892,000	$ 31,358,000	$ 31,830,000	$ 32,311,000	$ 32,798,000	$ 33,293,000	$ 33,795,000	$ 49,406,000
$ (10,699,000)	$ (11,260,000)	$ (11,430,000)	$ (11,602,000)	$ (11,777,000)	$ (11,955,000)	$ (12,135,000)	$ (12,318,000)	$ (12,504,000)	$ (18,280,000)
$ 18,218,000	$ 19,173,000	$ 19,462,000	$ 19,756,000	$ 20,053,000	$ 20,356,000	$ 20,663,000	$ 20,975,000	$ 21,291,000	$ 31,126,000
$ 19,282,000	$ 19,173,000	$ 19,462,000	$ 19,756,000	$ 20,053,000	$ 20,356,000	$ 20,663,000	$ 20,975,000	$ 21,291,000	$ 31,126,000
$ 20,882,000	$ 26,332,000	$ 31,143,000	$ 35,389,000	$ 39,137,000	$ 42,445,000	$ 45,365,000	$ 47,943,000	$ 50,218,000	$ 53,110,000

XII. CONCLUSIONS

After thorough investigation of the Shell carboxymethylation process, we have reached the conclusion that process would be a promising venture that would be best undertaken by a large corporation. The potential for a large profit combined with the competitive nature of the plastic industry lead us to this conclusion. A major chemical manufacturer would also have the advantages of possessing within the company a large funding base to subsidize the research and development and allocated utility facilities that would benefit a design such as this.

Based on our investigation of the uncertainties and assumptions that are a part of this plant design, we have devised several recommendations should this design be studied further.

First, a more thorough understanding of the reaction kinetics is essential to the carboxymethylation process. References contained in U.S. Patent #5,719,313 to kinetics are vague. A series of experiments were conducted, and several reaction parameters were varied from trial to trial. Precise knowledge of the order of reaction and residence time required for a 99.9% conversion of MA to MMA is key to the reactor and associated heat exchanger design. For example, a 15-minute residence time would result in a reaction chamber that is 4 times smaller. On a grander scale, a reduced reaction time gives the design engineer more options when facing the problem of removing several million BTU/hr from the reaction vessel, such as the use of cold shots or interstage cooling. A reduced reaction time may also allow for smaller-scale units throughout the design due to a smaller methanol recycle. A better understanding of the reaction kinetics would allow the reactor to be designed more accurately.

The next set of recommended steps in studying this reaction involves the chemistry of methanol and carbon monoxide. Ethanol is a known impurity in 99.9% pure methanol, and it is reactive with CO to form propionic acid. The presence of additional corrosives within the system, even on the order of parts per million, may have a significant effect on the corrosion time of the carbon steel vessels. Experiments should be conducted with various grades of methanol to determine the corrosiveness of the reactor product stream. A helpful guide to the safety measures that must be taken in terms of vessel thickness in the presence of acids is contained in Craig and Anderson's *Handbook of Corrosion Data*.

A third key aspect of the design process is the controllability of the finalized design. Control systems are unique to each process, and careful considerations must be made when choosing one control scheme over another. Part of this decision must be focused on the economics and reliability of the control system being purchased. Several companies, such as Omega, Inc., offer a consultant's approach to process control, wherein the company examines the plant-wide control and offers a detailed solution down to the specific models of each control valve. Another less expensive approach would be to have the design engineer have a control scheme in mind as the process is being finalized, and have he or she choose the individual parts of the control scheme, as well as design the overall control. Economics of the control processes must be taken into consideration in future designs. During the pilot plant trials various control variables can be investigated and a control structure could be evaluated.

The replacement of catalyst in the carboxymethylation reactor is a key factor in the design of this process. For this design the catalyst was replaced monthly. The rate of

decay in catalyst activity has not been characterized. This should be examined further in the laboratory and pilot plant. The effect of catalyst replacement rate on IRR is significant. To maintain the IRR above 20% the catalyst must last more than 2 days between replacements (Appendix I).

Although it may be beyond the scope of a first-level design, the senior engineer may want to consider the possibility of a major research project with the aim of studying the effects of a packed bed palladium acetate catalyst on the carboxymethylation reaction. A solid catalyst support provides numerous advantages over a free-roaming liquid solution catalyst; the most prominent of these is the elimination of a recycle stream and the decreased cost of liquid catalyst separation. In addition, it would be worthwhile to study several different inhibition options. It is known that methyl methacrylate polymerizes by both free radical and anionic mechanisms. The prevention of such reactions is accomplished primarily by the addition of a radical scavenger. The possibility of a cheap alternative to 4-methoxyphenol is a subject worthy of further experimentation.

Keeping these considerations in mind, the evidence supporting the construction of a plant to produce 100 MM lbs./yr. of methyl methacrylate via the carboxymethylation process is strongly recommended. The most important factors in this decision are the 39.5% investor's rate of return combined with the added safety and environmental advantages over previously studied MMA production processes.

XIII. EQUATIONS AND NOMENCLATURE

NOTE: The following equations were used for calculations in the Excel® calculation sheets. The equation variables were generated from ASPEN® outputs. References to the below equations are made on the Excel® sheets.

Distillation Column Sizing

Kirkbride Approximation for Optimal Feed Tray Location:

$$\frac{Nr}{Ns} = \left[\left(\frac{Zhk,f}{Zlk,f} \right) \cdot \left(\frac{Xlk,b}{Xhk,d} \right)^2 \cdot \left(\frac{B}{D} \right) \right]^{0.206} \quad (1)$$

Where **Nr** is Trays in Rectifying Section and **Ns** is Trays in Stripping Section
hk = Heavy Key, lk = Light Key, f = Feed, B = bottoms, D = distillate, Z = mol fraction

Seader and Henley, p.456 (SH, 456)

Actual # Trays =# Trays/ Tray Efficiency (2)

Distillation Column Costing

Column (Vertical Vessel Section)

$$\mathbf{CBM = 1780\ L^{0.87}\ D^{1.23}\ [2.86 + 1.694\ F_M\ (10.01 - 7.408 \ln(P) + 1.395(\ln P)^2)]} \quad (3)$$

Where: L = height, D = diameter, P = pressure
F_M = Materials Factor (Fig. 9.3c, Seider,Seader,Lewin, 350)
F_{BM} = Bare Module Factor (Fig. 9.3d, SSL, 350)
F_p = Pressure Factor (Fig. 9.3c, SSL, 350)
C_p = CBM/FBM (Fig. 9.3b, SSL, 350)

Sieve Tray Section

$$\mathbf{CBM = (193.04 + 22.72D + 60.38D^2)\ F_{BM}\ N_{act}\ f_q} \quad (4)$$

Where: N_{act} = actual # trays,
F_q = quantity factor (=1 when N_{act}>20) (Fig. 9.4, SSL, 351)

Heat Exchanger Sizing

$$Ft = \frac{\sqrt{R^2+1} \cdot \ln\left(\frac{1-S}{1-R \cdot S}\right)}{(R-1) \cdot \ln\left(\frac{2 - S\left(R+1-\sqrt{R^2+1}\right)}{2 - S\left(R+1+\sqrt{R^2+1}\right)}\right)} \quad (5)$$

Where:

$$R = (T_{\text{hot in}} - T_{\text{hot out}}) / (T_{\text{cold out}} - T_{\text{cold in}}) \quad (5a)$$

$$S = (T_{\text{cold out}} - T_{\text{cold in}}) / (T_{\text{hot in}} - T_{\text{cold in}}) \quad (5b)$$

Ft = Tube Correction Factor
Seider, Seader, and Lewin, p.323 (SSL, 323)

$$\Delta T_{LM} = (\Delta T_1 - \Delta T_2) / \ln(\Delta T_1/\Delta T_2) \quad (6)$$

(SSL, 322)

$$Q = UA_iF_t\Delta T_{LM \text{ for countercurrent flow}} \quad (7)$$

where A_i = area, U= overall heat transfer coefficient
(SSL, 323) or

$Q = m\Delta H_{vap}$ where H_{vap} = Heat of Vaporization (STEAM) (7a)

$Q = mC_p\Delta T$ where C_p = Specific Heat Capacity (COOLONG WATER) (7b)

$A_{c,i} = F_i/\rho_i u_I$ Where u_i = linear velocity, $A_{c,i}$=total cross-sectional area, ρ_i= density (8)

$A_{cFo} = D_s / P_t{*}C{*}b$ Where D_s = Shell Diameter, where C = clearance, b= baffle space, A_{cFo}= area of crossectional flow on the outside (8a)

$N_t = 4A_{c,i} / \Pi d_i^2$ Where N_t = # tubes per pass, d_i = inside diameter (9)

$A_{t,i} = \Pi d_i L$ Where L = tube length, $A_{t,i}$ = inside area (10)

$n = A_i / A_{t,i} N_t$ Where n = # tube passes, (11)

(SSL, 326)

$$Nu = 0.023 \cdot \left(\frac{DG}{\mu}\right)^{0.8} \cdot \left(\frac{Cp\mu}{k}\right)^{0.4} \quad (12)$$

$$Nu = \frac{hD}{k} \quad (13)$$

Where: Nu = Nusselt Number, D=diameter, G=mass velocity, C_p=specific heat capacity, μ=viscosity, k=conductivity

And: Re = Reynolds Number = (DG/μ), Pr = Prandtl Number = ($Cp\mu/k$)

(SSL, 329)

$$Nu = 0.36 \cdot \left(\frac{DG}{\mu}\right)^{0.55} \cdot \left(\frac{Cp \cdot \mu}{k}\right)^{\frac{1}{3}} \cdot \left(\frac{\mu b}{\mu w}\right)^{0.14} \quad (14)$$

where: μb = bulk viscosity, μw = wall viscosity
(SSL, 331)

$$-\Delta P = \frac{Ks \cdot 2 \cdot Nr \cdot f \cdot Gs^2}{gc \cdot \rho \cdot \phi} \quad (15)$$

where: $-\Delta P$ = tube pressure drop, Nr = # tube rows,
Gs = mass velocity = mass flow/ cross-sectional area, ρ = density, $\phi = 1.02(\mu b/\mu w)^{0.14}$,
gc = 32.17 ftlbm/lbfs^2 , Ks = correction factor

$$K = (N_{Prb}/ N_{Prw})^{0.11} \quad (15a)$$

Where N_{Prb} = Prandtl # of bulk, N_{Prw} = Prandtl # of wall

$$f = b \cdot \left(\frac{Do \cdot Gs}{\mu}\right)^{-0.15} \quad (16)$$

where: $b = 0.23 + 0.11/(x_T - 1)^{1.08}$ For Triangular Pitch, x_T = ratio of pitch transverse to flow-to-tube outside diameter, D_o = outside diameter

(SSL, 332)

TABLES 8.4, 8.5 and 8.6 (SSL, 317,328,333 respectively) were also used for sizing

(16a)

A second pressure drop equation based on the Darcy Equation:

Where **Friction Factor** = $f = 0.25*(1.82*\log(Re) - 1.62)^{-2}$ (16b)

$$-\Delta P = \frac{2 \cdot f \cdot Go^2 \cdot Ds \cdot \left(\frac{Lt}{b} - 1\right)}{gc \cdot \rho o \cdot De} \quad (16c)$$

Where D = effective diameter, Lt=tube length, b= baffle spacing, Ds = shell diameter
Go = mass velocity, f=friction factor

$$\Delta P_t = Kp*Np*\Delta P \quad (16d)$$

Where: Np = number of passes, Kp =correction for passes

$$Gi = \frac{Fi}{Nt \cdot \Pi \cdot \frac{Di^2}{4}} \quad (16e)$$

Where: Gi = mass flow, Nt = number of tubes, Fi = mass flow

(SSL, 330)

Note: The design heuristics in SSL, Appendix 10 were used in conjunction with the above equations and most input values were generated by the HEATX sub-routine in ASPEN®, but the above equations were what the ASPEN® sizing calculations were based on.

Heat Exchanger Costing

Fp = Pressure Factor	(Fig. 9.1b, SSL, 340)	
F_M = Material Factor	(Fig. 9.1a, SSL, 340)	
F_{BM} = Bare Module Factor	(Fig. 9.1c, SSL, 340)	
Cp = Purchase Cost = C_{BM}/F_{BM}	(Fig. 9.1a, SSL, 340)	(17)

Pump Sizing

Shaft Work = (Flow Rate * ΔP) / Pump Efficiency (18)
(Ulrich, p.310)

Charts from CRC HANDBOOK pgs. 1023-1034 (18a)

$Ns = NQ^{0.5} / H^{0.75}$
Where: Ns = Specific Speed, N = rpm, Q = flow rate in gpm, H = head in ft-lb_f/lbm

Pump Costing

F_p = Pressure Factor	(Fig. 5-50, U, 310)	(19)
C_p = Purchase Cost	(Fig. 5-49, U, 310)	
F_M = Material Factor	(Fig. 5-49, U, 310)	
C_{BM} = Cp * F_{BM}	(Fig. 5-49, U, 310)	
F_{BM} = Bare Module Factor	(Fig. 9.5, SSL, 352)	

Blower Costing

$C_{BM} = 835\ W^{0.95}\ F_{BM}$ (20)
Where: W = Shaft Work
(SSL, 351)

Vertical and Horizontal Vessels (and Tanks) Sizing

$Cp = 1780L^{0.87}\ D^{1.23}$ (21)

Reflux Tanks sized based on residence time:

Volumetric Flow * Hold Up Time = Volume of Tank (22)

Superficial Velocity = $(\rho_L - \rho_V) / \rho_V$ (23)

Where: ρ_L = Liquid density , ρ_V = Vapor density

Vertical and Horizontal Vessels (and Tanks) Costing

For F_{BM}, Fp, F_M and C_{BM}: REFER TO EQUATION (3) , SAME AS VERTICAL VESSEL PORTION OF DISTILLATION COLUMN (24)

Storage Vessel Sizing

Storage Vessels were also sized based on inlet volumetric flow and storage time

Volume = Volumetric Flow * Storage Time (25)

Storage Vessel Costing

F_{BM} = Bare Module Factor (Fig. 5-61 U, 316) (26)
C_p = Purchase Cost (Fig. 5-61 U, 316)
$C_{BM} = C_p * F_{BM}$ (Fig. 5-61 U, 316)

Isomerization Reactor Sizing

This Reactor because of its design was sized as a Heat Exchanger. A simplified version of equation (7) was used to find Surface Area of Heat Transfer.

$$\mathbf{Q = UA(\Delta T_{LM})} \quad (27)$$

Where: U = overall Heat Transfer Coefficient, A = Surface Area of Heat Transfer
ΔT_{LM} = log mean temperature difference

Isomerization Reactor Costing

The Costing for this reactor was done the exact same way as a heat exchanger, REFER TO EQUATION **(17)**

(Area of heat transfer translates to cost from Ulrich Charts)

Carboxymethylation Reactor (Vessel Part without Attached Heat Exchanger) Sizing

This reactor was sized like a vessel, based on hold up time and volumetric flow rate

Reactor Volume = Volumetric Flow * Residence Time (1 hr) (28)
Diameter and Height were found by geometric equations:
- $\mathbf{V = \pi r^2 L}$; $\mathbf{D = 2r}$ (29)

Where: r = radius , L = height, D = diameter, V= volume

Carboxymethylation Reactor (Vessel Part without Attached Heat Exchanger) Costing

FBM, Cp, FM and Fp were found exactly the same way as a vertical vessel:
REFER TO EQUATION **(24)** or **(3)** (30)

Costing Time Adjustment

All charts used to cost are in terms of 1982 prices so to convert to 1999 prices, the following formula was used:

CBM 1999 = (CBM 1982 * INDEX) / 315
Where: **INDEX = 400** (31)

ASPEN®

ASPEN® PROGRAM SIZING AND OUTPUT (32)
Anything with this reference means that the sub-routines (RADFRAC, HEATX) produced the output variables. Variables such as tray sizing, tower diameter, temperatures, pressures would be some of the possible variables from ASPEN®'s output for the whole flow sheet.

NOTE: F_{BM} of Materials Made of Hastelloy – C = 10 * F_{BM} (Carbon Steel)
All Economic Calculations were in-built Visual Basic Programs in Excel®

Utilities

The heat balance (equations 7a & 7b) was used to determine the flow rates of cooling water and steam as well as the necessary refrigeration. ASPEN® calculated the electricity necessary to run pumps and blowers from the following equation

Electricity needed = Shaft work / mechanical efficiency (33)

Optimization

"Six – tenths rule" to approximate cost of plant based on a change is amount:

$(A1/A2) = (C1/C2)^{0.6}$ (34)

Where: A = amount, C = Cost
(Ulrich)

Agitator Sizing

Taken From Design Heuristics (Appendix X, SSL, 803) (35)

D = Diameter
Liquid level = D, impeller level above bottom = D/3, impeller blade width = D/15,
Impeller diameter = D/3
(SSL, 803)

Design Temperature and Pressure

Design T (°F) = Operating Temperature (°F) + 50 °F
Design P (psi) = Operating Pressure (psi) + 35 psi (36)

Other Heuristics From Seider Seader and Lewin (Appendix 10, p795-807) (37)

Functional Height (SSL, 798)
Wall Thickness (SSL,807)
Vessel Support Type (SSL, 807)

ECONOMIC ANALYSIS Visual Basic EXCEL program

Anything with this reference indicates that all values referenced were computed by a program in Microsoft Excel® which was titled ECONOMICS.XLS

- Developed by Holger Nickish, Chemical Engineering Department, Univ. of Penn. 1999

(38)

Process Control

Dr. W. Luyben lecture notes and handout (39)

NOMENCLATURE - used in course of report

M	-	thousand
MM	-	million

ACH	-	The process that uses Acetone Cyanohydrin and HCN
BCPPP	-	Bis(3-chlorophenyl)(2-pyridyl)phosphine
C_{TDC}	-	Cost of Total Depreciable Capital
HCN	-	Hydrogen Cyanide
MA	-	Methyl Acetylene
MC	-	Methyl Crotonate
MMA	-	Methyl Methacrylate
MSA	-	Methanesulfonic Acid
PD	-	Propadiene

XIV. ACKNOWLEDGEMENTS

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XVI. APPENDIX

A. Problem statement

9. Propyne to Methyl Methacrylate
(recommended by Bruce M. Vrana, DuPont)

Methyl methacrylate (MMA) is a monomer or comonomer in many polymers, most notably Plexiglas (R). The conventional process has many drawbacks, including the use of sulfuric acid as a catalyst. Most manufacturers neutralize the sulfuric acid with ammonia, producing byproduct ammonium sulfate which must be sold or disposed of. HCN is also used in the process, requiring the MMA plant to be linked to a source of hazardous HCN.

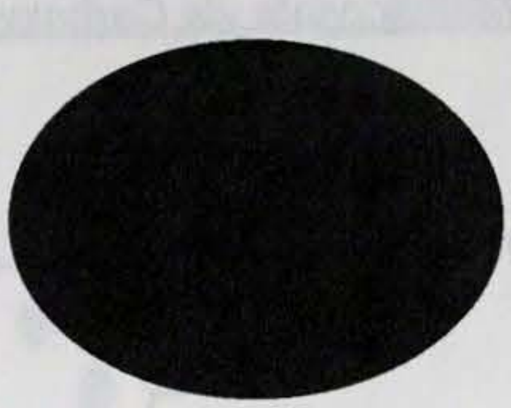
Shell has patented a new process with several advantages over conventional MMA processes. A major advantage is that neither HCN nor sulfuric acid are used. Shell found that propyne can be carbomethoxylated (reacted with CO and methanol) to produce MMA directly. The main disadvantage is that propyne is not normally considered a viable feedstock due to its scarcity and the impurities it contains. Shell's new catalyst tolerates impurities in the propyne much better than prior catalysts.

Your job is to develop a scenario for Shell to commercialize this process. You must first find a suitable feedstock for this process from the normal refinery and/or petrochemical streams available. Producing propyne to provide the feedstock is discouraged, due to high cost. Having found a stream which contains suitable quantities of propyne in high enough purity for this process to be feasible, design a plant to produce 100 MM lb/yr of MMA by the new Shell process. Determine the overall economic feasibility of the plant.

The plant design should be as environmentally friendly as possible. Recover and recycle process chemicals to the maximum economic extent. Also, energy consumption should be minimized, to the extent economically justified. The plant design must also be controllable and safe to operate.

Assume a U.S. Gulf Coast location on the same site as a large oil and petrochemical plant. MMA can be sold or transferred for $0.60/lb, according to your marketing organization. Value the propyne as appropriate for alternative uses for the stream (i.e., if the stream you are using is normally burned, value the propyne at fuel value). A major gas vendor is willing to locate across the fence from you and supply CO at the required pressure for $0.12/lb. Your marketing organization projects that the long-term average price of methanol is $0.40/gal.

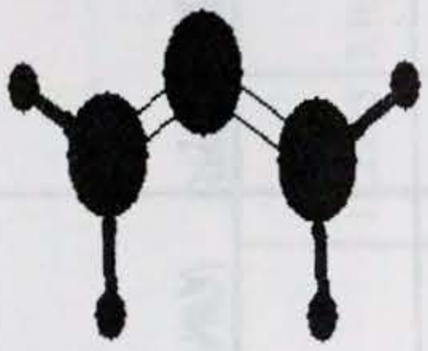
B. Chemical Reactions

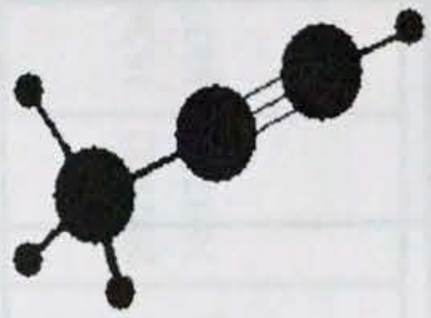


K_2CO_3 on γ - Alumina

(1) $H_2C{=}C{=}CH_2 \longrightarrow H_3C{-}C{\equiv}CH$

Propadiene **Methyl Acetylene**

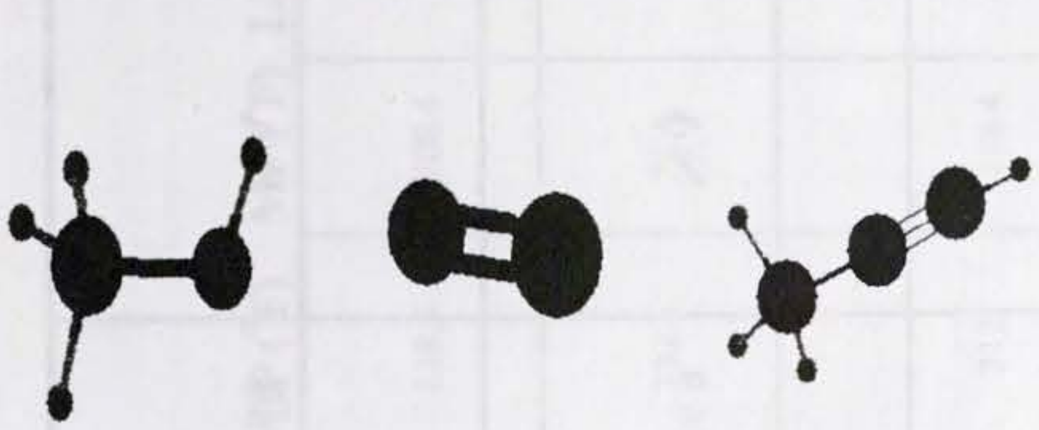


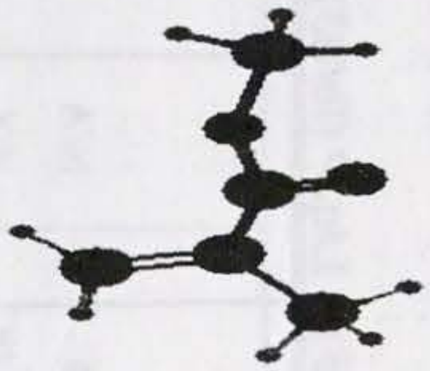


Pd(II)Ac + MSA + BCPPP

(2) $CH_3OH + CO + H_3C{-}C{\equiv}CH \longrightarrow C_5H_8O_2$

Methanol **Carbon Monoxide** **Methyl Acetylene** **Methyl Methacrylate**

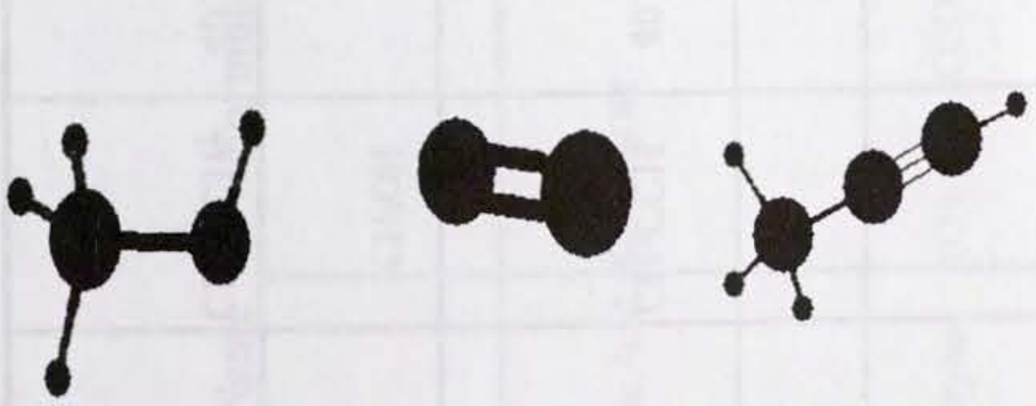


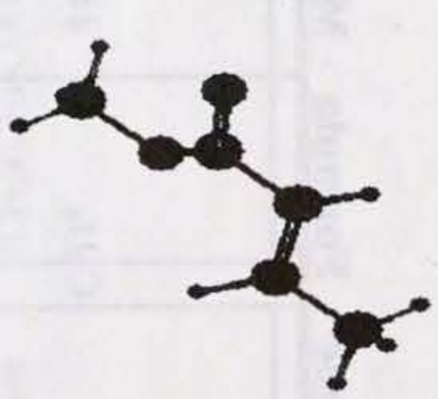


Pd(II)Ac + MSA + BCPPP

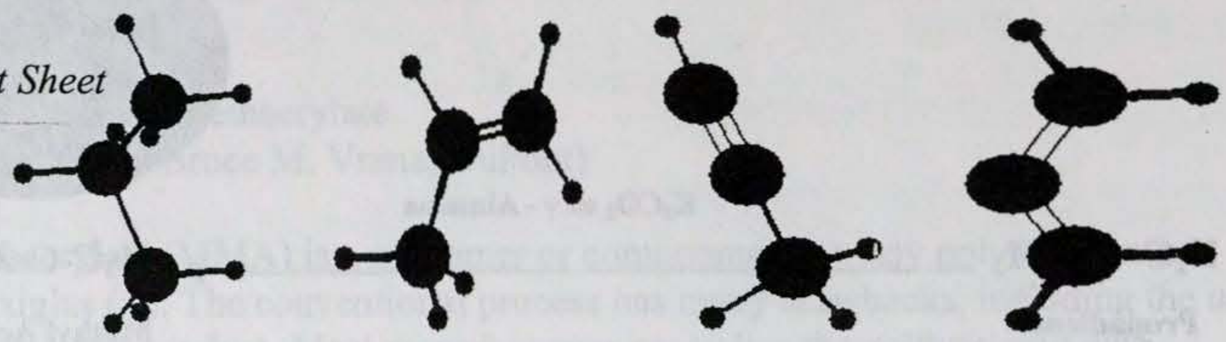
(3) $CH_3OH + CO + H_3C{-}C{\equiv}CH \longrightarrow C_5H_8O_2$

Methanol **Carbon Monoxide** **Methyl Acetylene** **Methyl Crotonate Isomer**





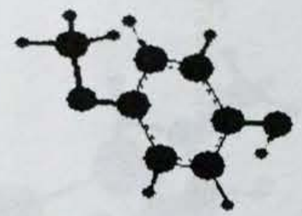
C. Chemical Fact Sheet

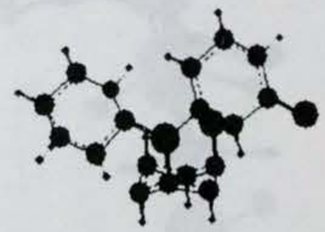


Chemical Name	Formula	MW	BP (^{o}F)	MP (^{o}F)	Liq. ρ (lb/ft3)	Vap. ρ (lb/ft3)	Risk	Safety
Propane	C_3H_8	44.1	-107.8	-370.4	N/A	1.5	12	9,16
Propylene	C_3H_6	42.8	-117.9	-365	N/A	1.5	12	9,16,33
Methylacetylene	CH_3CCH	40.1	-73.8	-216.9	N/A	N/A	37	38,36
Propadiene	CH_2CCH_2	40.1	-93.2	-276.8	N/A	1.42	N/A	16,33,38

Chemical Name	Formula	MW	BP (°F)	MP (°F)	Liq. ρ (lb/ft3)	Vap. ρ (lb/ft3)	Risk	Safety
Methanol	CH_3OH	32.04	148.5	-208.4	78.92	68.67	11,23/25	7,16,24,45
Methanesulfonic Acid	CH_3SO_2OH	96.1	332.6	N/A	42.15	3.3	34	26,36,45
Methyl Methacrylate	$(CH_3)(CH_2)CCOOCH_3$	100.12	212	-118.4	66.7	3.5	36/37/38 11,43	9,16,29,33
Methyl Crotonate	$(CH_3)(CH)_2COOCH_3$	100.12	246.2	N/A	66.13	N/A	20/21/22 36/37/38	16,26,33 36/37/39

Chemical Name	Formula	MW	BP (°F)	MP (°F)	Liq. ρ (lb/ft3)	Vap. ρ (lb/ft3)	Risk	Safety
4-methoxyphenol	$(C_6H_4OH)OCH_3$	124.14	469.4	132.8	N/A	4.3	20/21/22 36/37/38,41	26,36
Palladium (II) Acetate	$Pd(CH_3COOH)_2$	224.5	N/A	N/A	N/A	N/A	41	---
Bis-(3-chlorophenyl) (2-pyridyl)phosphine	$(C_6H_4Cl)_2(C_5NH_4)P$	332.2					36/37/38*	26,37/39*
Carbon Monoxide	CO	28.01	N/A	N/A	N/A	N/A	61,12,23 48/23	53,45
Water/Steam	H_2O	18.02	212	100	62.1 at 90 °F	0.4 at 175 psi	---	---





* indicates the risk and safety data was taken for (tris 4chlorophenyl phosphine), a similar molecule.

Risk Warning Legend:

11	Highly flammable
12	Extremely flammable
20	Harmful by inhalation
21	Harmful in contact with skin
22	Harmful if swallowed
23	Toxic by inhalation
25	Toxic if swallowed
26	Very toxic by inhalation
34	Causes burns
36	Irritating to the eyes
37	Irritating to the respiratory system
38	Irritating to the skin
41	Risk of serious damage to eyes
43	May cause sensitization by skin contact
45	May cause cancer
48	Danger of serious damage to health by prolonged exposure
61	May cause harm to the unborn child

Safety Warning Legend:

7	Keep container tightly closed
9	Keep container in a well ventilated place
16	Keep away from sources of ignition -- no smoking
22	Do not breathe dust
24	Avoid contact with the skin
26	In case of contact with eyes, rinse immediately with plenty of water and seek medical advice
29	Do not empty into drains
33	Take precautionary measures against static discharges
36	Wear suitable protective clothing
37	Wear suitable gloves
38	In case of insufficient ventilation, wear suitable respiratory equipment
39	Wear eye/face protection
45	In case of accident, or if you feel unwell, seek medical advice immediately (show label)
53	Avoid exposure -- obtain special instruction before use

D. Material Safety Data Sheets

1. Bis(3-chlorophenyl)(2-pyridyl)phosphine

SAFETY DATA IS NOT AVAILABLE FOR THIS COMPONENT

2. Carbon Monoxide

CHEMICAL IDENTIFICATION

CATALOG #: 486116
NAME: CARBON-12C MONOXIDE-16O, 13C&18O-DEPLETED, 99.9 ATOM % 12C, 99.95 ATOM % 16O

COMPOSITION/INFORMATION ON INGREDIENTS

CAS #: 630-08-0
MF: CO
EC NO: 211-128-3
SYNONYMS
CARBONE (OXYDE DE) (FRENCH) * CARBONIC OXIDE * CARBONIO (OSSIDO DI) (ITALIAN) * CARBON MONOXIDE (ACGIH:OSHA) * CARBON OXIDE (CO) * EXHAUST GAS * FLUE GAS * KOHLENMONOXID (GERMAN) * KOHLENOXYD (GERMAN) * KOOLMONOXYDE (DUTCH) * OXYDE DE CARBONE (FRENCH) * WEGLA TLENEK (POLISH) *

HAZARDS IDENTIFICATION

LABEL PRECAUTIONARY STATEMENTS
FLAMMABLE (USA)
HIGHLY FLAMMABLE (EU)
TOXIC
TOXIC BY INHALATION.
POSSIBLE RISK OF HARM TO THE UNBORN CHILD.
CALIF. PROP. 65 REPRODUCTIVE HAZARD.
TARGET ORGAN(S):
BLOOD
NERVES
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE IMMEDIATELY (SHOW THE LABEL WHERE POSSIBLE).
WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES AND EYE/FACE PROTECTION.
DO NOT BREATHE VAPOR.
CYLINDER TEMPERATURE SHOULD NOT EXCEED 125 F(52 C).
DO NOT PUNCTURE OR INCINERATE THIS CYLINDER.
CONTENTS UNDER PRESSURE.

FIRST-AID MEASURES

IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
CALL A PHYSICIAN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
CALL A PHYSICIAN.

FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA
DO NOT EXTINGUISH BURNING GAS IF FLOW CANNOT BE SHUT OFF IMMEDIATELY.
USE WATER SPRAY OR FOG NOZZLE TO KEEP CYLINDER COOL. MOVE CYLINDER AWAY FROM FIRE IF THERE IS NO RISK.
SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.

FLAMMABLE GAS.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
MAY FORM EXPLOSIVE MIXTURES WITH AIR.
VAPOR MAY TRAVEL CONSIDERABLE DISTANCE TO SOURCE OF IGNITION AND FLASH BACK.

ACCIDENTAL RELEASE MEASURES

EVACUATE AREA.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
SHUT OFF LEAK IF THERE IS NO RISK.
VENTILATE THE SPILL SITE THOROUGHLY BEFORE REENTERING.

HANDLING AND STORAGE

REFER TO NEXT SECTION.
ADDITIONAL INFORMATION
CARBON MONOXIDE REACTS EXPLOSIVELY WITH BROMINE TRIFLUORIDE, BROMINE PENTAFLUORIDE, CHLORINE DIOXIDE OR PEROXODISULFURYL DIFLUORIDE. IT REACTS WITH SODIUM OR POTASSIUM METAL PRODUCING EXPLOSIVE METAL CARBONYLS. EXPLOSIONS HAVE REPORTED ON CHARGING CARBON MONOXIDE INTO A MIXTURE OF FLUORINE AND OXYGEN. ALUMINUM POWDER BURNS IN CARBON MONOXIDE AND ACCELERATES TO INCANDESCENCE IN THE PRESENCE OF ALUMINUM HALIDE VAPORS. CARBON MONOXIDE IGNITES ON CONTACT WITH IODINE HEPTAFLUORIDE. INCOMPATIBLE WITH SILVER(I) OXIDE OR IRON(III) OXIDE.

EXPOSURE CONTROLS/PERSONAL PROTECTION

CHEMICAL SAFETY GOGGLES.
COMPATIBLE CHEMICAL-RESISTANT GLOVES.
NIOSH/MSHA-APPROVED RESPIRATOR IN NONVENTILATED AREAS AND/OR FOR EXPOSURE ABOVE THE ACGIH TLV.
MECHANICAL EXHAUST REQUIRED.
SAFETY SHOWER AND EYE BATH.
DO NOT BREATHE GAS.
DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
WASH THOROUGHLY AFTER HANDLING.
TOXIC.
POSSIBLE TERATOGEN.
KEEP TIGHTLY CLOSED.
KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.
STORE AND USE WITH ADEQUATE VENTILATION.

STABILITY AND REACTIVITY

STABILITY
STABLE.
INCOMPATIBILITIES
SODIUM
POTASSIUM
STRONG OXIDIZING AGENTS
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS
TOXIC FUMES OF:
CARBON MONOXIDE, CARBON DIOXIDE
HAZARDOUS POLYMERIZATION
WILL NOT OCCUR.

TOXICOLOGICAL INFORMATION

ACUTE EFFECTS
MAY BE FATAL IF INHALED.
EXPOSURE CAN CAUSE:
NAUSEA, DIZZINESS AND HEADACHE
CHRONIC EFFECTS
BLOOD EFFECTS
NEUROTOXIC EFFECTS
POSSIBLE TERATOGEN.
RTECS #: FG3500000
CARBON MONOXIDE
TOXICITY DATA

IHL-MAN LCLO:4000 PPM/30M	29ZWAE -,207,1968
IHL-HMN LCLO:5000 PPM/5M	TABIA2 3,231,1933
IHL-RAT LC50:1807 PPM/4H	TXAPA9 17,752,1970
IHL-MUS LC50:2444 PPM/4H	TXAPA9 17,752,1970
IHL-GPG LC50:5718 PPM/4H	TXAPA9 17,752,1970
IHL-BWD LC50:1334 PPM	AECTCV 12,355,1983

TARGET ORGAN DATA
BEHAVIORAL (CHANGE IN PSYCHOPHYSIOLOGICAL TESTS)
BLOOD (METHEMOGLOBINEMIA-CARBOXHEMOGLOBINEMIA)
EFFECTS ON FERTILITY (POST-IMPLANTATION MORTALITY)
EFFECTS ON EMBRYO OR FETUS (FETOTOXICITY)
SPECIFIC DEVELOPMENTAL ABNORMALITIES (MUSCULOSKELETAL SYSTEM)
SPECIFIC DEVELOPMENTAL ABNORMALITIES (CARDIOVASCULAR SYSTEM)
SPECIFIC DEVELOPMENTAL ABNORMALITIES (IMMUNE AND RETICULOENDOTHELIAL SYST
EFFECTS ON NEWBORN (STILLBIRTH)
EFFECTS ON NEWBORN (VIABILITY INDEX)
EFFECTS ON NEWBORN (GROWTH STATISTICS)
EFFECTS ON NEWBORN (BEHAVIORAL)
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.

DISPOSAL CONSIDERATIONS

BURN IN A CHEMICAL INCINERATOR EQUIPPED WITH AN AFTERBURNER AND SCRUBBER BUT EXERT EXTRA CARE IN IGNITING AS THIS MATERIAL IS HIGHLY FLAMMABLE.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

REGULATORY INFORMATION

EUROPEAN INFORMATION
EC INDEX NO: 006-001-00-2
HIGHLY FLAMMABLE
TOXIC
R 61
MAY CAUSE HARM TO THE UNBORN CHILD.
R 12
EXTREMELY FLAMMABLE.
R 23
TOXIC BY INHALATION.
R 48/23
TOXIC: DANGER OF SERIOUS DAMAGE TO HEALTH BY PROLONGED EXPOSURE

THROUGH INHALATION.
S 53
AVOID EXPOSURE - OBTAIN SPECIAL INSTRUCTIONS BEFORE USE.
S 45
IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE IMMEDIATELY (SHOW THE LABEL WHERE POSSIBLE).
REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
ACGIH TLV-TWA 29 MG/M3 (25 PPM) DTLVS* TLV/BEI,1997
MSHA STANDARD-AIR:TWA 50 PPM (55 MG/M3)
DTLVS* 3,41,1971
OSHA PEL (GEN INDU):8H TWA 50 PPM (55 MG/M3)
CFRGBR 29,1910.1000,1994
OSHA PEL (CONSTRUC):8H TWA 50 PPM (55 MG/M3)
CFRGBR 29,1926.55,1994
OSHA PEL (SHIPYARD):8H TWA 50 PPM (55 MG/M3)
CFRGBR 29,1915.1000,1993
OSHA PEL (FED CONT):8H TWA 50 PPM (55 MG/M3)
CFRGBR 41,50-204.50,1994
NIOSH REL TO CARBON MONOXIDE-AIR:8H TWA 35 PPM;CL 200 PPM
NIOSH* DHHS #92-100,1992
NOHS 1974: HZD 17460; NIS 43; TNF 2593; NOS 68; TNE 32958
NOES 1983: HZD 17460; NIS 24; TNF 1950; NOS 52; TNE 68434; TFE 7860
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY
EPA TSCA SECTION 8(D) UNPUBLISHED HEALTH/SAFETY STUDIES
EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JUNE 1998
NIOSH ANALYTICAL METHOD, 1996: CARBON MONOXIDE, 6604

3. Methanesulfonic Acid

CHEMICAL IDENTIFICATION

CATALOG #: M6391
NAME: METHANESULFONIC ACID

COMPOSITION/INFORMATION ON INGREDIENTS

CAS #: 75-75-2
MF: CH4O3S
EC NO: 200-898-6
SYNONYMS
KYSELINA METHANSULFONOVA (CZECH) * METHYLSULFONIC ACID *

HAZARDS IDENTIFICATION

LABEL PRECAUTIONARY STATEMENTS
TOXIC
TOXIC BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.
CAUSES BURNS.
IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF WATER AND SEEK MEDICAL ADVICE.
TAKE OFF IMMEDIATELY ALL CONTAMINATED CLOTHING.
WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES AND EYE/FACE PROTECTION.
IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE IMMEDIATELY (SHOW THE LABEL WHERE POSSIBLE).

FIRST-AID MEASURES

IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES OR SKIN WITH COPIOUS AMOUNTS OF WATER FOR AT LEAST 15 MINUTES WHILE REMOVING CONTAMINATED CLOTHING AND SHOES.
ASSURE ADEQUATE FLUSHING OF THE EYES BY SEPARATING THE EYELIDS WITH FINGERS.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
CALL A PHYSICIAN.
DISCARD CONTAMINATED CLOTHING AND SHOES.

FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA
WATER SPRAY.
CARBON DIOXIDE, DRY CHEMICAL POWDER OR APPROPRIATE FOAM.
SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
EMITS TOXIC FUMES UNDER FIRE CONDITIONS.

ACCIDENTAL RELEASE MEASURES

EVACUATE AREA.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
COVER WITH DRY LIME OR SODA ASH, PICK UP, KEEP IN A CLOSED CONTAINER AND HOLD FOR WASTE DISPOSAL.

VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

HANDLING AND STORAGE

REFER TO NEXT SECTION.

ADDITIONAL INFORMATION

CONTAINS LESS THAN 2PPM METHYL METHANESULFONATE, WHICH IS A CARCINOGEN.

EXPOSURE CONTROLS/PERSONAL PROTECTION

WEAR APPROPRIATE NIOSH/MSHA-APPROVED RESPIRATOR, CHEMICAL-RESISTANT GLOVES, SAFETY GOGGLES, OTHER PROTECTIVE CLOTHING.
USE ONLY IN A CHEMICAL FUME HOOD.
SAFETY SHOWER AND EYE BATH.
FACESHIELD (8-INCH MINIMUM).
DO NOT BREATHE VAPOR.
DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
WASH THOROUGHLY AFTER HANDLING.
KEEP TIGHTLY CLOSED.
STORE IN A COOL DRY PLACE.

PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AND ODOR

COLORLESS VISCOUS LIQUID OR SOLID

PHYSICAL PROPERTIES

BOILING POINT: 167 C/10MM.
FLASHPOINT >230F >110C
VAPOR PRESSURE: 1MM 20 C
SPECIFIC GRAVITY: 1.481
VAPOR DENSITY: 3.3

STABILITY AND REACTIVITY

INCOMPATIBILITIES

BASES
AMINES
STRONG REDUCING AGENTS
CORRODES STEEL

HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS

TOXIC FUMES OF:
CARBON MONOXIDE, CARBON DIOXIDE
SULFUR OXIDES

TOXICOLOGICAL INFORMATION

ACUTE EFFECTS

HARMFUL IF SWALLOWED, INHALED, OR ABSORBED THROUGH SKIN.
MATERIAL IS EXTREMELY DESTRUCTIVE TO TISSUE OF THE MUCOUS MEMBRANES AND UPPER RESPIRATORY TRACT, EYES AND SKIN.
INHALATION MAY RESULT IN SPASM, INFLAMMATION AND EDEMA OF THE LARYNX AND BRONCHI, CHEMICAL PNEUMONITIS AND PULMONARY EDEMA.
SYMPTOMS OF EXPOSURE MAY INCLUDE BURNING SENSATION, COUGHING, WHEEZING, LARYNGITIS, SHORTNESS OF BREATH, HEADACHE, NAUSEA AND VOMITING.
TO THE BEST OF OUR KNOWLEDGE, THE CHEMICAL, PHYSICAL, AND TOXICOLOGICAL PROPERTIES HAVE NOT BEEN THOROUGHLY INVESTIGATED.

RTECS #: PB1140000
METHANESULFONIC ACID

TOXICITY DATA
ORL-RAT LD50:200 MG/KG KODAK* 21MAY1971
SKN-GPG LD50:>2 GM/KG KODAK* 21MAY1971
ORL-QAL LD50:1 GM/KG JRPFA4 48,371,1976
ADDITIONAL INFORMATION
ORL-RAT LD50:200-400 MG/KG.
SKN-RBT LD50:>200 MG/KG (10% MSA)
SKN-RBT LD50:2000 MG/KG
IHL-RBT LC50:>330 PPM
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.

DISPOSAL CONSIDERATIONS

DISSOLVE OR MIX THE MATERIAL WITH A COMBUSTIBLE SOLVENT AND BURN IN A CHEMICAL INCINERATOR EQUIPPED WITH AN AFTERBURNER AND SCRUBBER. OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

REGULATORY INFORMATION

EUROPEAN INFORMATION
EC INDEX NO: 607-145-00-4
TOXIC
R 34
CAUSES BURNS.
S 26
IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF WATER AND SEEK MEDICAL ADVICE.
S 36
WEAR SUITABLE PROTECTIVE CLOTHING.
S 45
IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE IMMEDIATELY (SHOW THE LABEL WHERE POSSIBLE).
REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
NOHS 1974: HZD 83577; NIS 3; TNF 82; NOS 9; TNE 1209
NOES 1983: HZD 83577; NIS 7; TNF 325; NOS 13; TNE 8084; TFE 1393
EPA GENETOX PROGRAM 1988, INCONCLUSIVE: E COLI POLA WITHOUT S9
EPA GENETOX PROGRAM 1988, INCONCLUSIVE: D MELANOGASTER SEX-LINKED LETHAL
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY
EPA TSCA SECTION 8(D) UNPUBLISHED HEALTH/SAFETY STUDIES
EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JUNE 1998

4. Methanol

CHEMICAL IDENTIFICATION

CATALOG #: M1775
NAME: METHANOL, ABSOLUTE ACETONE FREE

COMPOSITION/INFORMATION ON INGREDIENTS

CAS #: 67-56-1
EC NO: 200-659-6
SYNONYMS
ALCOOL METHYLIQUE (FRENCH) * ALCOOL METILICO (ITALIAN) * CARBINOL * COLONIAL SPIRIT * COLUMBIAN SPIRIT * METANOLO (ITALIAN) * METHANOL (ACGIH) * METHYL ALCOHOL (DOT:OSHA) * METHYLOL * METHYLALKOHOL (GERMAN) * METHYL HYDRATE * METHYL HYDROXIDE * METYLOWY ALKOHOL (POLISH) * MONOHYDROXYMETHANE * PYROXYLIC SPIRIT * RCRA WASTE NUMBER U154 * WOOD ALCOHOL * WOOD NAPHTHA * WOOD SPIRIT *

HAZARDS IDENTIFICATION

LABEL PRECAUTIONARY STATEMENTS
FLAMMABLE (USA)
HIGHLY FLAMMABLE (EU)
TOXIC
TOXIC BY INHALATION AND IF SWALLOWED.
IRRITATING TO EYES AND SKIN.
TARGET ORGAN(S):
EYES
KIDNEYS
KEEP CONTAINER TIGHTLY CLOSED.
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
AVOID CONTACT WITH SKIN.
IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE IMMEDIATELY (SHOW THE LABEL WHERE POSSIBLE).

FIRST-AID MEASURES

IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES OR SKIN WITH COPIOUS AMOUNTS OF WATER FOR AT LEAST 15 MINUTES WHILE REMOVING CONTAMINATED CLOTHING AND SHOES.
ASSURE ADEQUATE FLUSHING OF THE EYES BY SEPARATING THE EYELIDS WITH FINGERS.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS. CALL A PHYSICIAN.
DISCARD CONTAMINATED CLOTHING AND SHOES.

FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA
CARBON DIOXIDE, DRY CHEMICAL POWDER OR APPROPRIATE FOAM.
SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
EXTREMELY FLAMMABLE.
VAPOR MAY TRAVEL CONSIDERABLE DISTANCE TO SOURCE OF IGNITION AND

FLASH BACK.

ACCIDENTAL RELEASE MEASURES

EVACUATE AREA.
SHUT OFF ALL SOURCES OF IGNITION.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
COVER WITH DRY-LIME, SAND, OR SODA ASH. PLACE IN COVERED CONTAINERS USING NON-SPARKING TOOLS AND TRANSPORT OUTDOORS.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

HANDLING AND STORAGE

REFER TO NEXT SECTION.

EXPOSURE CONTROLS/PERSONAL PROTECTION

WEAR APPROPRIATE NIOSH/MSHA-APPROVED RESPIRATOR, CHEMICAL-RESISTANT GLOVES, SAFETY GOGGLES, OTHER PROTECTIVE CLOTHING.
MECHANICAL EXHAUST REQUIRED.
SAFETY SHOWER AND EYE BATH.
DO NOT BREATHE VAPOR.
AVOID CONTACT WITH EYES, SKIN AND CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
DO NOT USE IF SKIN IS CUT OR SCRATCHED. WASH THOROUGHLY AFTER HANDLING.
TOXIC.
IRRITANT.
KEEP TIGHTLY CLOSED.
KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.
STORE IN A COOL DRY PLACE.

PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AND ODOR
LIQUID.
PHYSICAL PROPERTIES
BOILING POINT: 64.7 C
MELTING POINT: -98 C
FLASHPOINT 52F
11.11C
EXPLOSION LIMITS IN AIR:
UPPER 36%
LOWER 6%
AUTOIGNITION TEMPERATURE: 725 F 384C
VAPOR PRESSURE: 97.68MM 20 C 410MM 50 C
SPECIFIC GRAVITY: 0.791
VAPOR DENSITY: 1.1

STABILITY AND REACTIVITY

STABILITY
STABLE.
INCOMPATIBILITIES
ACIDS
ACID CHLORIDES
ACID ANHYDRIDES
OXIDIZING AGENTS
REDUCING AGENTS

ALKALI METALS
PROTECT FROM MOISTURE.
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS
TOXIC FUMES OF:
CARBON MONOXIDE, CARBON DIOXIDE
HAZARDOUS POLYMERIZATION
WILL NOT OCCUR.

TOXICOLOGICAL INFORMATION

ACUTE EFFECTS
HARMFUL IF INHALED.
HARMFUL IF SWALLOWED.
MAY BE HARMFUL IF ABSORBED THROUGH THE SKIN.
CAUSES EYE AND SKIN IRRITATION.
MATERIAL MAY BE IRRITATING TO MUCOUS MEMBRANES AND UPPER RESPIRATORY TRACT.
EXPOSURE CAN CAUSE:
GASTROINTESTINAL DISTURBANCES
MAY CAUSE CONVULSIONS.
TARGET ORGAN(S):
EYES
KIDNEYS
LIVER
HEART
RTECS #: PC1400000
METHANOL
IRRITATION DATA

SKN-RBT 20 MG/24H MOD	85JCAE -,187,1986
EYE-RBT 40 MG MOD	UCDS** 3/24/1970
EYE-RBT 100 MG/24H MOD	85JCAE -,187,1986

TOXICITY DATA

ORL-MAN LDLO:6422 MG/KG	CMAJAX 128,14,1983
ORL-HMN LDLO:428 MG/KG	NPIRI* 1,74,1974
ORL-HMN LDLO:143 MG/KG	34ZIAG -,382,1969
UNR-MAN LDLO:868 MG/KG	85DCAI 2,73,1970
ORL-RAT LD50:5628 MG/KG	GTPZAB 19(11),27,1975
IHL-RAT LC50:64000 PPM/4H	NPIRI* 1,74,1974
IPR-RAT LD50:7529 MG/KG	EVHPAZ 61,321,1985
IVN-RAT LD50:2131 MG/KG	EVHPAZ 61,321,1985
ORL-MUS LD50:7300 MG/KG	TXCYAC 25,271,1982
IPR-MUS LD50:10765 MG/KG	EVHPAZ 61,321,1985
SCU-MUS LD50:9800 MG/KG	TXAPA9 18,185,1971
IVN-MUS LD50:4710 MG/KG	EVHPAZ 61,321,1985
ORL-MKY LD50:7 GM/KG	TXAPA9 3,202,1961
ORL-RBT LD50:14200 MG/KG	FAONAU 48A,105,1970
SKN-RBT LD50:15800 MG/KG	NPIRI* 1,74,1974
IPR-RBT LD50:1826 MG/KG	EVHPAZ 61,321,1985
IVN-RBT LD50:8907 MG/KG	EVHPAZ 61,321,1985
IPR-GPG LD50:3556 MG/KG	EVHPAZ 61,321,1985
IPR-HAM LD50:8555 MG/KG	EVHPAZ 61,321,1985

TARGET ORGAN DATA
SENSE ORGANS AND SPECIAL SENSES (OPTIC NERVE NEUROPATHY)
SENSE ORGANS AND SPECIAL SENSES (VISUAL FIELD CHANGES)
BEHAVIORAL (HEADACHE)
LUNGS, THORAX OR RESPIRATION (DYSPNAE)
LUNGS, THORAX OR RESPIRATION (OTHER CHANGES)

GASTROINTESTINAL (NAUSEA OR VOMITING)
SPECIFIC DEVELOPMENTAL ABNORMALITIES (CENTRAL NERVOUS SYSTEM)
SPECIFIC DEVELOPMENTAL ABNORMALITIES (MUSCULOSKELETAL SYSTEM)
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.

DISPOSAL CONSIDERATIONS

BURN IN A CHEMICAL INCINERATOR EQUIPPED WITH AN AFTERBURNER AND SCRUBBER BUT EXERT EXTRA CARE IN IGNITING AS THIS MATERIAL IS HIGHLY FLAMMABLE.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

REGULATORY INFORMATION

EUROPEAN INFORMATION
EC INDEX NO: 603-001-00-X
HIGHLY FLAMMABLE
TOXIC
R 11
HIGHLY FLAMMABLE.
R 23/25
TOXIC BY INHALATION AND IF SWALLOWED.
S 7
KEEP CONTAINER TIGHTLY CLOSED.
S 16
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
S 24
AVOID CONTACT WITH SKIN.
S 45
IN CASE OF ACCIDENT OR IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE IMMEDIATELY (SHOW THE LABEL WHERE POSSIBLE).

REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
ACGIH TLV-STEL 328 MG/M3 (250 PPM) (SKIN) DTLVS* TLV/BEI,1997
ACGIH TLV-TWA 262 MG/M3 (200 PPM) DTLVS* TLV/BEI,1997
EPA FIFRA 1988 PESTICIDE SUBJECT TO REGISTRATION OR RE-REGISTRATION
FEREAC 54,7740,1989
MSHA STANDARD-AIR:TWA 200 PPM (260 MG/M3) (SKIN)
DTLVS* 3,155,1971
OSHA PEL (GEN INDU):8H TWA 200 PPM (260 MG/M3)
CFRGBR 29,1910.1000,1994
OSHA PEL (CONSTRUC):8H TWA 200 PPM (260 MG/M3)
CFRGBR 29,1926.55,1994
OSHA PEL (SHIPYARD):8H TWA 200 PPM (260 MG/M3)
CFRGBR 29,1915.1000,1993
OSHA PEL (FED CONT):8H TWA 200 PPM (260 MG/M3)
CFRGBR 41,50-204.50,1994
NIOSH REL TO METHANOL-AIR:10H TWA 200 PPM (SK);STEL 250 PPM (SK)
NIOSH* DHHS #92-100,1992
NOHS 1974: HZD 45930; NIS 344; TNF 78840; NOS 203; TNE 737242
NOES 1983: HZD 45930; NIS 373; TNF 101075; NOS 225; TNE 1620617; TFE 388352
EPA GENETOX PROGRAM 1988, NEGATIVE: SHE-CLONAL ASSAY; CELL TRANSFORM.-SA7/SHE
EPA GENETOX PROGRAM 1988, NEGATIVE: N CRASSA-ANEUPLOIDY; IN VITRO

SCE-NONHUMAN
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY
EPA TSCA SECTION 8(D) UNPUBLISHED HEALTH/SAFETY STUDIES
EPA TSCA SECTION 8(E) RISK NOTIFICATION, 8EHQ-0892-8989
ON EPA IRIS DATABASE
EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JUNE 1998
NIOSH ANALYTICAL METHOD, 1994: METHANOL, 2000
NIOSH ANALYTICAL METHOD, 1996: VOLATILE ORGANIC COMPOUND, 2549
U.S. INFORMATION
THIS PRODUCT IS SUBJECT TO SARA SECTION 313 REPORTING REQUIREMENTS.

5. 4-methoxyphenol

CHEMICAL IDENTIFICATION

CATALOG #: M18655
NAME: 4-METHOXYPHENOL, 99%

COMPOSITION/INFORMATION ON INGREDIENTS

CAS #: 150-76-5
MF: C7H8O2
EC NO: 205-769-8
SYNONYMS
P-GUAIACOL * HYDROQUINONE MONOMETHYL ETHER * HYDROXYANISOLE * P-HYDROXYANISOLE * 4-HYDROXYANISOLE * P-HYDROXYMETHOXYBENZENE * LEUCOBASAL * LEUCODINE B * MECHINOLUM * MEQUINOL * P-METHOXYPHENOL * 4-METHOXYPHENOL (ACGIH) * MONO METHYL ETHER HYDROQUINONE * NOVO-DERMOQUINONA * PMF (ANTIOXIDANT) * USAF AN-7 *

HAZARDS IDENTIFICATION

LABEL PRECAUTIONARY STATEMENTS
TOXIC (USA)
HARMFUL (EU)
HARMFUL BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.
IRRITATING TO EYES, RESPIRATORY SYSTEM AND SKIN.
RISK OF SERIOUS DAMAGE TO EYES.
IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF WATER AND SEEK MEDICAL ADVICE.
WEAR SUITABLE PROTECTIVE CLOTHING.

FIRST-AID MEASURES

IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES OR SKIN WITH COPIOUS AMOUNTS OF WATER FOR AT LEAST 15 MINUTES WHILE REMOVING CONTAMINATED CLOTHING AND SHOES.
ASSURE ADEQUATE FLUSHING OF THE EYES BY SEPARATING THE EYELIDS WITH FINGERS.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
CALL A PHYSICIAN.
DISCARD CONTAMINATED CLOTHING AND SHOES.

FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA
CARBON DIOXIDE, DRY CHEMICAL POWDER OR APPROPRIATE FOAM.
SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.

ACCIDENTAL RELEASE MEASURES

EVACUATE AREA.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
COVER WITH DRY-LIME, SAND, OR SODA ASH. PLACE IN COVERED CONTAINERS USING NON-SPARKING TOOLS AND TRANSPORT OUTDOORS.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

HANDLING AND STORAGE

REFER TO NEXT SECTION.

EXPOSURE CONTROLS/PERSONAL PROTECTION

LONG RUBBER OR NEOPRENE GAUNTLET GLOVES.
CHEMICAL SAFETY GOGGLES.
NIOSH/MSHA-APPROVED RESPIRATOR.
USE ONLY IN A CHEMICAL FUME HOOD.
FACESHIELD (8-INCH MINIMUM).
SAFETY SHOWER AND EYE BATH.
DO NOT BREATHE VAPOR.
DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
WASH THOROUGHLY AFTER HANDLING.
TOXIC.
IRRITANT.
KEEP TIGHTLY CLOSED.
STORE IN A COOL DRY PLACE.

PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AND ODOR
WHITE TO OFF-WHITE CRYSTALLINE CHIPS
PHYSICAL PROPERTIES
BOILING POINT: 243 C
MELTING POINT: 55 C TO 57 C
FLASHPOINT >230
109C
AUTOIGNITION TEMPERATURE: 789 F 420C
VAPOR PRESSURE: <0.01MM 20 C
VAPOR DENSITY: 4.3

STABILITY AND REACTIVITY

INCOMPATIBILITIES

BASES
ACID CHLORIDES
ACID ANHYDRIDES
OXIDIZING AGENTS
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS
TOXIC FUMES OF:
CARBON MONOXIDE, CARBON DIOXIDE

TOXICOLOGICAL INFORMATION

ACUTE EFFECTS
HARMFUL IF SWALLOWED, INHALED, OR ABSORBED THROUGH SKIN.
CAUSES SEVERE EYE IRRITATION.
CAUSES SKIN IRRITATION.
MATERIAL IS IRRITATING TO MUCOUS MEMBRANES AND UPPER
RESPIRATORY TRACT.
DEPENDING ON THE INTENSITY AND DURATION OF EXPOSURE, EFFECTS MAY
VARY FROM MILD IRRITATION TO SEVERE DESTRUCTION OF TISSUE.
PROLONGED CONTACT CAN CAUSE:
DAMAGE TO THE EYES
SEVERE IRRITATION OR BURNS.
TO THE BEST OF OUR KNOWLEDGE, THE CHEMICAL, PHYSICAL, AND

TOXICOLOGICAL PROPERTIES HAVE NOT BEEN THOROUGHLY INVESTIGATED.
RTECS #: SL7700000
PHENOL, P-METHOXY-
IRRITATION DATA
SKN-RBT 6 GM/12D-I MLD JIHTAB 31,79,1949
TOXICITY DATA
ORL-RAT LD50:1600 MG/KG KODAK* 21MAY1971
IPR-MUS LD50:250 MG/KG NTIS** AD691-490
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.

DISPOSAL CONSIDERATIONS

DISSOLVE OR MIX THE MATERIAL WITH A COMBUSTIBLE SOLVENT AND BURN IN A CHEMICAL INCINERATOR EQUIPPED WITH AN AFTERBURNER AND SCRUBBER. OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

REGULATORY INFORMATION

EUROPEAN INFORMATION
HARMFUL
R 20/21/22
HARMFUL BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.
R 36/37/38
IRRITATING TO EYES, RESPIRATORY SYSTEM AND SKIN.
R 41
RISK OF SERIOUS DAMAGE TO EYES.
S 26
IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF WATER AND SEEK MEDICAL ADVICE.
S 36
WEAR SUITABLE PROTECTIVE CLOTHING.
REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
ACGIH TLV-TWA 5 MG/M3 DTLVS* TLV/BEI,1997
NIOSH REL TO 4-METHOXYPHENOL-AIR:10H TWA 5 MG/M3
NIOSH* DHHS #92-100,1992
NOES 1983: HZD X3672; NIS 136; TNF 9805; NOS 89; TNE 250087; TFE 49763
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY
EPA TSCA SECTION 8(D) UNPUBLISHED HEALTH/SAFETY STUDIES
EPA TSCA SECTION 8(E) RISK NOTIFICATION, 8EHQ-0892-8789;8EHQ-0892-8802
EPA TSCA SECTION 8(E) RISK NOTIFICATION, 8EHQ-0892-8825
EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JUNE 1998

6. Methyl acetylene

CHEMICAL IDENTIFICATION

CATALOG #: 480983
NAME: PROPYNE, 98%

COMPOSITION/INFORMATION ON INGREDIENTS

CAS #: 74-99-7
MF: C3H4
EC NO: 200-828-4

SYNONYMS

ACETYLENE, METHYL- * ALLYLENE * METHYL ACETYLENE (ACGIH:OSHA) *
PROPINE * PROPYNE (OSHA) * 1-PROPYNE (9CI) *

HAZARDS IDENTIFICATION

LABEL PRECAUTIONARY STATEMENTS

FLAMMABLE (USA)
HIGHLY FLAMMABLE (EU)
IRRITANT
IRRITATING TO RESPIRATORY SYSTEM.
DANGER: FLAMMABLE GAS UNDER PRESSURE.
IN CASE OF INSUFFICIENT VENTILATION, WEAR SUITABLE RESPIRATORY EQUIPMENT.
WEAR SUITABLE PROTECTIVE CLOTHING.
CYLINDER TEMPERATURE SHOULD NOT EXCEED 125 F(52 C).
DO NOT PUNCTURE OR INCINERATE THIS CYLINDER.
REFRIGERATE.
STORE AWAY FROM HEAT.

FIRST-AID MEASURES

IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES WITH COPIOUS AMOUNTS OF WATER FOR AT LEAST 15 MINUTES.
IN CASE OF CONTACT, IMMEDIATELY WASH SKIN WITH SOAP AND COPIOUS AMOUNTS OF WATER.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS. CALL A PHYSICIAN.

FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA

DO NOT EXTINGUISH BURNING GAS IF FLOW CANNOT BE SHUT OFF IMMEDIATELY.
USE WATER SPRAY OR FOG NOZZLE TO KEEP CYLINDER COOL. MOVE CYLINDER AWAY FROM FIRE IF THERE IS NO RISK.

SPECIAL FIREFIGHTING PROCEDURES

WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.
DANGER: FLAMMABLE GAS UNDER PRESSURE.

UNUSUAL FIRE AND EXPLOSIONS HAZARDS

MAY FORM EXPLOSIVE MIXTURES WITH AIR.
VAPOR MAY TRAVEL CONSIDERABLE DISTANCE TO SOURCE OF IGNITION AND FLASH BACK.

ACCIDENTAL RELEASE MEASURES

EVACUATE AREA AND KEEP PERSONNEL UPWIND.
SHUT OFF ALL SOURCES OF IGNITION.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
SHUT OFF LEAK IF THERE IS NO RISK.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

EXPOSURE CONTROLS/PERSONAL PROTECTION

CHEMICAL SAFETY GOGGLES.
COMPATIBLE CHEMICAL-RESISTANT GLOVES.
NIOSH/MSHA-APPROVED RESPIRATOR IN NONVENTILATED AREAS AND/OR FOR EXPOSURE ABOVE THE ACGIH TLV.
MECHANICAL EXHAUST REQUIRED.
SAFETY SHOWER AND EYE BATH.
DO NOT BREATHE GAS.
DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
WASH THOROUGHLY AFTER HANDLING.
KEEP TIGHTLY CLOSED.
KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.
CYLINDER TEMPERATURE SHOULD NOT EXCEED 125 F(52 C).
STORE AND USE WITH ADEQUATE VENTILATION.
CONTENTS UNDER PRESSURE.
USE WITH EQUIPMENT RATED FOR CYLINDER PRESSURE, AND OF COMPATIBLE MATERIALS OF CONSTRUCTION. CLOSE VALVE WHEN NOT IN USE AND WHEN EMPTY.
MAKE SURE CYLINDER IS PROPERLY SECURED WHEN IN USE OR STORED.
DO NOT PUNCTURE OR INCINERATE THIS CYLINDER.
NO-DEPOSIT, NO-RETURN CYLINDER, DO NOT REUSE.

PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL PROPERTIES
BOILING POINT: -23.2 C
MELTING POINT: -102.7 C
VAPOR PRESSURE: 204.6MM 49.5 C

STABILITY AND REACTIVITY

STABILITY
CAN DECOMPOSE EXPLOSIVELY AT 4.5-5.6 ATMOSPHERES PRESSURE.
INCOMPATIBILITIES
STRONG OXIDIZING AGENTS
OXYGEN
STORE AWAY FROM HEAT.
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS
CARBON MONOXIDE, CARBON DIOXIDE

TOXICOLOGICAL INFORMATION

ACUTE EFFECTS
MAY BE HARMFUL IF INHALED.
MATERIAL IS IRRITATING TO MUCOUS MEMBRANES AND UPPER RESPIRATORY TRACT.
CAN CAUSE RAPID SUFFOCATION.
PROLONGED EXPOSURE CAN CAUSE:
NARCOTIC EFFECT

SYMPTOMS OF OVEREXPOSURE MAY INCLUDE RAPID RESPIRATION, DIMINISHED MENTAL ALERTNESS, FAULTY JUDGEMENT, RAPID FATIGUE, NAUSEA, LOSS OF CONSCIOUSNESS, COMA AND POSSIBLY DEATH.
CAN CAUSE SEVERE FROSTBITE.
RTECS #: UK4250000
PROPYNE
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.

DISPOSAL CONSIDERATIONS

CAUTION: NO-RETURN CYLINDER. DO NOT REUSE. EMPTY CYLINDER WILL CONTAIN HAZARDOUS RESIDUE. FOLLOW PROPER DISPOSAL TECHNIQUES.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

REGULATORY INFORMATION

EUROPEAN INFORMATION
HIGHLY FLAMMABLE
IRRITANT
R 37
IRRITATING TO RESPIRATORY SYSTEM.
HIGHLY FLAMMABLE
S 38
IN CASE OF INSUFFICIENT VENTILATION, WEAR SUITABLE RESPIRATORY EQUIPMENT.
S 36
WEAR SUITABLE PROTECTIVE CLOTHING.
REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
ACGIH TLV-TWA 1640 MG/M3 (1000 PPM) DTLVS* TLV/BEI,1997
MSHA STANDARD-AIR:TWA 1000 PPM (1650 MG/M3)
DTLVS* 3,153,1971
OSHA PEL (GEN INDU):8H TWA 1000 PPM (1650 MG/M3)
CFRGBR 29,1910.1000,1994
OSHA PEL (CONSTRUC):8H TWA 1000 PPM (1650 MG/M3)
CFRGBR 29,1926.55,1994
OSHA PEL (SHIPYARD):8H TWA 1000 PPM (1650 MG/M3)
CFRGBR 29,1915.1000,1993
OSHA PEL (FED CONT):8H TWA 1000 PPM (1650 MG/M3)
CFRGBR 41,50-204.50,1994
NIOSH REL TO METHYL ACETYLENE-AIR:10H TWA 1000 PPM
NIOSH* DHHS #92-100,1992
NOHS 1974: HZD 46435; NIS 9; TNF 311; NOS 13; TNE 5033
NOES 1983: HZD 46435; NIS 1; TNF 3; NOS 7; TNE 119; TFE 6
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY
EPA TSCA SECTION 8(D) UNPUBLISHED HEALTH/SAFETY STUDIES
EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JUNE 1998

7. Methyl Crotonate

CHEMICAL IDENTIFICATION

CATALOG #: 139459
NAME: METHYL CROTONATE, 98%

COMPOSITION/INFORMATION ON INGREDIENTS

CAS #: 623-43-8
MF: C5H8O2
EC NO: 210-793-7
SYNONYMS
TRANS-2-BUTENOIC ACID METHYL ESTER * (E)-CROTONIC ACID METHYL ESTER * METHYL TRANS-2-BUTENOATE * METHYL CROTONATE * METHYL ALPHA-CROTONATE * METHYL E-CROTONATE * METHYL TRANS-CROTONATE *

HAZARDS IDENTIFICATION

LABEL PRECAUTIONARY STATEMENTS
FLAMMABLE (USA)
HIGHLY FLAMMABLE (EU)
HARMFUL
HARMFUL BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.
IRRITATING TO EYES, RESPIRATORY SYSTEM AND SKIN.
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
TAKE PRECAUTIONARY MEASURES AGAINST STATIC DISCHARGES.
IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF WATER AND SEEK MEDICAL ADVICE.
WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES AND EYE/FACE PROTECTION.

FIRST-AID MEASURES

IN CASE OF CONTACT, IMMEDIATELY WASH SKIN WITH SOAP AND COPIOUS AMOUNTS OF WATER.
IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES WITH COPIOUS AMOUNTS OF WATER FOR AT LEAST 15 MINUTES.
ASSURE ADEQUATE FLUSHING OF THE EYES BY SEPARATING THE EYELIDS WITH FINGERS.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
CALL A PHYSICIAN.
REMOVE AND WASH CONTAMINATED CLOTHING PROMPTLY.

FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA
CARBON DIOXIDE, DRY CHEMICAL POWDER OR APPROPRIATE FOAM.
SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.
USE WATER SPRAY TO COOL FIRE-EXPOSED CONTAINERS.
WARNING:
FLAMMABLE LIQUID.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
VAPOR MAY TRAVEL CONSIDERABLE DISTANCE TO SOURCE OF IGNITION AND FLASH BACK.

CONTAINER EXPLOSION MAY OCCUR UNDER FIRE CONDITIONS.

ACCIDENTAL RELEASE MEASURES

EVACUATE AREA.
SHUT OFF ALL SOURCES OF IGNITION.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
COVER WITH AN ACTIVATED CARBON ADSORBENT, TAKE UP AND PLACE IN CLOSED CONTAINERS. TRANSPORT OUTDOORS.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

HANDLING AND STORAGE

REFER TO NEXT SECTION.

EXPOSURE CONTROLS/PERSONAL PROTECTION

CHEMICAL SAFETY GOGGLES.
COMPATIBLE CHEMICAL-RESISTANT GLOVES.
RUBBER APRON.
SAFETY SHOWER AND EYE BATH.
MECHANICAL EXHAUST REQUIRED.
NIOSH/MSHA-APPROVED RESPIRATOR.
DO NOT BREATHE VAPOR.
DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
WASH THOROUGHLY AFTER HANDLING.
IRRITANT.
HARMFUL LIQUID AND FUMES.
KEEP TIGHTLY CLOSED.
KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.
STORE IN A COOL DRY PLACE.

PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AND ODOR
COLORLESS LIQUID
PHYSICAL PROPERTIES
BOILING POINT: 118 C TO 120 C
FLASHPOINT 40 F
4C
SPECIFIC GRAVITY: 0.944

STABILITY AND REACTIVITY

INCOMPATIBILITIES
OXIDIZING AGENTS
BASES
ACIDS
HEAT
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS
TOXIC FUMES OF:
CARBON MONOXIDE, CARBON DIOXIDE

TOXICOLOGICAL INFORMATION

ACUTE EFFECTS
HARMFUL IF SWALLOWED.
MAY BE HARMFUL IF INHALED.
MAY BE HARMFUL IF ABSORBED THROUGH THE SKIN.

VAPOR OR MIST IS IRRITATING TO THE EYES, MUCOUS MEMBRANES AND UPPER RESPIRATORY TRACT.
CAUSES SKIN IRRITATION.
SYMPTOMS OF EXPOSURE MAY INCLUDE BURNING SENSATION, COUGHING, WHEEZING, LARYNGITIS, SHORTNESS OF BREATH, HEADACHE, NAUSEA AND VOMITING.
RTECS #: GQ5710000
CROTONIC ACID, METHYL ESTER, (E)-
IRRITATION DATA
SKN-RBT 500 MG/24H MOD FCTXAV 17,865,1979
TOXICITY DATA
ORL-RAT LD50:>3200 MG/KG FCTXAV 17,865,1979
ORL-MUS LD50:1600 MG/KG FCTXAV 17,865,1979
SKN-RBT LD50:>5 GM/KG FCTXAV 17,865,1979
SKN-GPG LD50:10 ML/KG FCTXAV 17,865,1979
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.

DISPOSAL CONSIDERATIONS

BURN IN A CHEMICAL INCINERATOR EQUIPPED WITH AN AFTERBURNER AND SCRUBBER BUT EXERT EXTRA CARE IN IGNITING AS THIS MATERIAL IS HIGHLY FLAMMABLE.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

REGULATORY INFORMATION

EUROPEAN INFORMATION
HIGHLY FLAMMABLE
HARMFUL
R 20/21/22
HARMFUL BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.
R 36/37/38
IRRITATING TO EYES, RESPIRATORY SYSTEM AND SKIN.
HIGHLY FLAMMABLE
S 16
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
S 33
TAKE PRECAUTIONARY MEASURES AGAINST STATIC DISCHARGES.
S 26
IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF WATER AND SEEK MEDICAL ADVICE.
S 36/37/39
WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES AND EYE/FACE PROTECTION.
REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY

8. Methyl Methacrylate

CHEMICAL IDENTIFICATION

CATALOG #: M55909
NAME: METHYL METHACRYLATE, 99%

COMPOSITION/INFORMATION ON INGREDIENTS

CAS #: 80-62-6
MF: C5H8O2
EC NO: 201-297-1
SYNONYMS
ACRYLIC ACID, 2-METHYL-, METHYL ESTER * METAKRYLAN METYLU (POLISH) * METHACRYLATE DE METHYLE (FRENCH) * METHACRYLSAEUREMETHYL ESTER (GERMAN) * 2-(METHOXYCARBONYL)-1-PROPENE * METHYLESTER KYSELINY METHAKRYLOVE (CZECH) * METHYLMETHACRYLAAT (DUTCH) * METHYL-METHACRYLAT (GERMAN) * METHYL METHACRYLATE (ACGIH:OSHA) * METHYL METHACRYLATE MONOMER * METHYL METHYLACRYLATE * METHYL ALPHA-METHYLACRYLATE * METHYL 2-METHYL-2-PROPENOATE * 2-METHYL-2-PROPENOIC ACID METHYL ESTER * METIL METACRILATO (ITALIAN) * NCI-C50680 * PEGALAN * 2-PROPENOIC ACID, 2-METHYL-, METHYL ESTER * RCRA WASTE NUMBER U162 *

HAZARDS IDENTIFICATION

LABEL PRECAUTIONARY STATEMENTS
FLAMMABLE (USA)
HIGHLY FLAMMABLE (EU)
CORROSIVE
CAUSES BURNS.
MAY CAUSE SENSITIZATION BY INHALATION AND SKIN CONTACT.
LACHRYMATOR.
TARGET ORGAN(S):
NOSE
LIVER
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
KEEP CONTAINER TIGHTLY CLOSED IN A COOL WELL-VENTILATED PLACE.
IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF WATER AND SEEK MEDICAL ADVICE.
WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES AND EYE/FACE PROTECTION.

FIRST-AID MEASURES

IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES OR SKIN WITH COPIOUS AMOUNTS OF WATER FOR AT LEAST 15 MINUTES WHILE REMOVING CONTAMINATED CLOTHING AND SHOES.
ASSURE ADEQUATE FLUSHING OF THE EYES BY SEPARATING THE EYELIDS WITH FINGERS.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
CALL A PHYSICIAN IMMEDIATELY.
DISCARD CONTAMINATED SHOES.

FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA

CARBON DIOXIDE, DRY CHEMICAL POWDER OR APPROPRIATE FOAM.
SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.
USE WATER SPRAY TO COOL FIRE-EXPOSED CONTAINERS.
FLAMMABLE LIQUID.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
VAPOR MAY TRAVEL CONSIDERABLE DISTANCE TO SOURCE OF IGNITION AND FLASH BACK.
MAY UNDERGO AUTOPOLYMERIZATION.
CONTAINER EXPLOSION MAY OCCUR UNDER FIRE CONDITIONS.

ACCIDENTAL RELEASE MEASURES

EVACUATE AREA.
SHUT OFF ALL SOURCES OF IGNITION.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
COVER WITH AN ACTIVATED CARBON ADSORBENT, TAKE UP AND PLACE IN CLOSED CONTAINERS. TRANSPORT OUTDOORS.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

HANDLING AND STORAGE

REFER TO NEXT SECTION.
ADDITIONAL INFORMATION
METHYL METHACRYLATE IS INHIBITED WITH 10 PPM HYDROQUINONE MONOMETHYL ETHER. DO NOT STORE UNDER INERT ATMOSPHERE. IT IS ADVISABLE TO USE MATERIAL WITHIN 6 MONTHS.

EXPOSURE CONTROLS/PERSONAL PROTECTION

CHEMICAL SAFETY GOGGLES.
WEAR HEAVY RUBBER GLOVES.
SAFETY SHOWER AND EYE BATH.
FACESHIELD (8-INCH MINIMUM).
USE ONLY IN A CHEMICAL FUME HOOD.
NIOSH/MSHA-APPROVED RESPIRATOR.
DO NOT BREATHE VAPOR.
DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
WASH THOROUGHLY AFTER HANDLING.
CORROSIVE.
LACHRYMATOR.
SENSITIZER.
KEEP TIGHTLY CLOSED.
KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.

PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AND ODOR
COLORLESS LIQUID
PHYSICAL PROPERTIES
BOILING POINT: 100 C
MELTING POINT: -48 C
FLASHPOINT 50 F
9C
EXPLOSION LIMITS IN AIR:
UPPER 12.5%

LOWER 2.12%
AUTOIGNITION TEMPERATURE: 815 F 434C
VAPOR PRESSURE: 29MM 20 C
SPECIFIC GRAVITY: 0.936
VAPOR DENSITY: 3.5

STABILITY AND REACTIVITY

INCOMPATIBILITIES
OXIDIZING AGENTS
PEROXIDES
BASES
ACIDS
REDUCING AGENTS
AMINES
HALOGENS
HEAT
MAY POLYMERIZE ON EXPOSURE TO LIGHT.
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS
TOXIC FUMES OF:
CARBON MONOXIDE, CARBON DIOXIDE

TOXICOLOGICAL INFORMATION

ACUTE EFFECTS
HARMFUL IF SWALLOWED, INHALED, OR ABSORBED THROUGH SKIN.
MATERIAL IS EXTREMELY DESTRUCTIVE TO TISSUE OF THE MUCOUS MEMBRANES AND UPPER RESPIRATORY TRACT, EYES AND SKIN.
INHALATION MAY RESULT IN SPASM, INFLAMMATION AND EDEMA OF THE LARYNX AND BRONCHI, CHEMICAL PNEUMONITIS AND PULMONARY EDEMA.
SYMPTOMS OF EXPOSURE MAY INCLUDE BURNING SENSATION, COUGHING, WHEEZING, LARYNGITIS, SHORTNESS OF BREATH, HEADACHE, NAUSEA AND VOMITING.
MAY CAUSE ALLERGIC RESPIRATORY AND SKIN REACTIONS.
PROLONGED EXPOSURE CAN CAUSE:
NARCOTIC EFFECT
TARGET ORGAN(S):
NOSE
LIVER, KIDNEYS
RTECS #: OZ5075000
METHACRYLIC ACID, METHYL ESTER
IRRITATION DATA

SKN-RBT 10 GM/KG OPEN	JIHTAB 23,343,1941
EYE-RBT 150 MG	INMEAF 14,292,1945

TOXICITY DATA

ORL-RAT LD50:7872 MG/KG	JIHTAB 23,343,1941
IHL-RAT LC50:78000 MG/M3/4H	GTPZAB 20(6),5,1976
IPR-RAT LD50:1328 MG/KG	JDREAF 51,1632,1972
SCU-RAT LD50:7088 MG/KG	INMEAF 14,292,1945
ORL-MUS LD50:3625 MG/KG	GISAAA 41(4),6,1976
IHL-MUS LC50:18500 MG/M3/2H	GTPZAB 20(6),5,1976
IPR-MUS LD50:945 MG/KG	INMEAF 14,292,1945
SCU-MUS LD50:5954 MG/KG	INMEAF 14,292,1945
ORL-DOG LD50:4725 MG/KG	INMEAF 14,292,1945
SCU-DOG LD50:4252 MG/KG	INMEAF 14,292,1945
ORL-RBT LD50:8700 MG/KG	GISAAA 41(4),6,1976

SKN-RBT LD50:>5 GM/KG	NTIS** OTS0544282
ORL-GPG LD50:5954 MG/KG	INMEAF 14,292,1945
IPR-GPG LD50:1890 MG/KG	INMEAF 14,292,1945
SCU-GPG LD50:5954 MG/KG	INMEAF 14,292,1945
IHL-MAM LC50:20 GM/M3	GISAAA 51(5),61,1986

TARGET ORGAN DATA
BEHAVIORAL (SLEEP)
BEHAVIORAL (SOMNOLENCE)
BEHAVIORAL (EXCITEMENT)
BEHAVIORAL (ANOREXIA, HUMAN)
EFFECTS ON EMBRYO OR FETUS (FETOTOXICITY)
SPECIFIC DEVELOPMENTAL ABNORMALITIES (OTHER DEVELOPMENTAL ABNORMALITIES)
TUMORIGENIC (EQUIVOCAL TUMORIGENIC AGENT BY RTECS CRITERIA)
TUMORIGENIC (TUMORS AT SITE OF APPLICATION)
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.

DISPOSAL CONSIDERATIONS

BURN IN A CHEMICAL INCINERATOR EQUIPPED WITH AN AFTERBURNER AND SCRUBBER BUT EXERT EXTRA CARE IN IGNITING AS THIS MATERIAL IS HIGHLY FLAMMABLE.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

REGULATORY INFORMATION

EUROPEAN INFORMATION
EC INDEX NO: 607-035-00-6
HIGHLY FLAMMABLE
CORROSIVE
R 11
HIGHLY FLAMMABLE.
R 36/37/38
IRRITATING TO EYES, RESPIRATORY SYSTEM AND SKIN.
R 43
MAY CAUSE SENSITIZATION BY SKIN CONTACT.
S 9
KEEP CONTAINER IN A WELL-VENTILATED PLACE.
S 16
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
S 29
DO NOT EMPTY INTO DRAINS.
S 33
TAKE PRECAUTIONARY MEASURES AGAINST STATIC DISCHARGES.
REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
ACGIH TLV-NOT CLASSIFIABLE AS A HUMAN CARCINOGEN DTLVS* TLV/BEI,1997
ACGIH TLV-TWA 410 MG/M3 (100 PPM) DTLVS* TLV/BEI,1997
IARC CANCER REVIEW:ANIMAL INADEQUATE EVIDENCE IMEMDT 19,187,1979
IARC CANCER REVIEW:HUMAN NO ADEQUATE DATA IMEMDT 19,187,1979
IARC CANCER REVIEW:HUMAN INADEQUATE EVIDENCE IMEMDT 60,445,1994
IARC CANCER REVIEW:ANIMAL LACK CARCINOGENICITYIMEMDT 60,445,1994
IARC CANCER REVIEW:GROUP 3 IMEMDT 60,445,1994
MSHA STANDARD-AIR:TWA 100 PPM (410 MG/M3)

DTLVS* 3,168,1971
OSHA PEL (GEN INDU):8H TWA 100 PPM (410 MG/M3)
CFRGBR 29,1910.1000,1994
OSHA PEL (CONSTRUC):8H TWA 100 PPM (410 MG/M3)
CFRGBR 29,1926.55,1994
OSHA PEL (SHIPYARD):8H TWA 100 PPM (410 MG/M3)
CFRGBR 29,1915.1000,1993
OSHA PEL (FED CONT):8H TWA 100 PPM (410 MG/M3)
CFRGBR 41,50-204.50,1994
NIOSH REL TO METHYL METHACRYLATE-AIR:10H TWA 100 PPM
NIOSH* DHHS #92-100,1992
NOHS 1974: HZD 47700; NIS 89; TNF 11522; NOS 73; TNE 89435
NOES 1983: HZD 47700; NIS 76; TNF 6757; NOS 80; TNE 170079; TFE 59519
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY
EPA TSCA 8(A) PRELIMINARY ASSESSMENT INFORMATION, FINAL RULE
FEREAC 47,26992,82
EPA TSCA SECTION 8(D) UNPUBLISHED HEALTH/SAFETY STUDIES
ON EPA IRIS DATABASE
EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JUNE 1998
NIOSH ANALYTICAL METHOD, 1994: METHYL METHACRYLATE, 2537
NTP CARCINOGENESIS STUDIES (INHALATION);NO EVIDENCE:MOUSE,RAT
NTPTR* NTP-TR-314,86
U.S. INFORMATION
THIS PRODUCT IS SUBJECT TO SARA SECTION 313 REPORTING REQUIREMENTS.

9. Palladium Acetate

CHEMICAL IDENTIFICATION

CATALOG #: 379875
NAME: PALLADIUM(II) ACETATE, 99.98%

COMPOSITION/INFORMATION ON INGREDIENTS

CAS #: 3375-31-3
MF: C2H4O2
EC NO: 222-164-4
SYNONYMS
ACETIC ACID PALLADIUM SALT * BIS(ACETATO)PALLADIUM *
BISACETYLPALLADIUM * DIACETATOPALLADIUM * DIACETOXYPALLADIUM *
PALLADIUM(2+) ACETATE * PALLADIUM DIACETATE * PALLADIUM(II) ACETATE *
PALLADOUS ACETATE *

HAZARDS IDENTIFICATION

DATA NOT AVAILABLE

FIRST-AID MEASURES

IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES WITH COPIOUS AMOUNTS OF WATER FOR AT LEAST 15 MINUTES.
IN CASE OF CONTACT, IMMEDIATELY WASH SKIN WITH SOAP AND COPIOUS AMOUNTS OF WATER.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS. CALL A PHYSICIAN.
WASH CONTAMINATED CLOTHING BEFORE REUSE.

FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA
WATER SPRAY.
CARBON DIOXIDE, DRY CHEMICAL POWDER OR APPROPRIATE FOAM.
SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
EMITS TOXIC FUMES UNDER FIRE CONDITIONS.

ACCIDENTAL RELEASE MEASURES

WEAR RESPIRATOR, CHEMICAL SAFETY GOGGLES, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
SWEEP UP, PLACE IN A BAG AND HOLD FOR WASTE DISPOSAL.
AVOID RAISING DUST.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

HANDLING AND STORAGE

REFER TO NEXT SECTION.

EXPOSURE CONTROLS/PERSONAL PROTECTION

CHEMICAL SAFETY GOGGLES.
COMPATIBLE CHEMICAL-RESISTANT GLOVES.
NIOSH/MSHA-APPROVED RESPIRATOR.

SAFETY SHOWER AND EYE BATH.
MECHANICAL EXHAUST REQUIRED.
AVOID INHALATION.
AVOID CONTACT WITH EYES, SKIN AND CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
WASH THOROUGHLY AFTER HANDLING.
KEEP TIGHTLY CLOSED.
STORE IN A COOL DRY PLACE.

PHYSICAL AND CHEMICAL PROPERTIES

DATA NOT AVAILABLE

STABILITY AND REACTIVITY

INCOMPATIBILITIES
STRONG OXIDIZING AGENTS
HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS
TOXIC FUMES OF:
CARBON MONOXIDE, CARBON DIOXIDE

TOXICOLOGICAL INFORMATION

ACUTE EFFECTS
MAY BE HARMFUL BY INHALATION, INGESTION, OR SKIN ABSORPTION.
MAY CAUSE EYE IRRITATION.
MAY CAUSE SKIN IRRITATION.
TO THE BEST OF OUR KNOWLEDGE, THE CHEMICAL, PHYSICAL, AND
TOXICOLOGICAL PROPERTIES HAVE NOT BEEN THOROUGHLY INVESTIGATED.
RTECS #: AJ1900000
ACETIC ACID, PALLADIUM(2+) SALT
TOXICITY DATA
ORL-MUS LD50:2100 MG/KG GISAAA 51(12),88,1986
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES
(RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR
COMPLETE INFORMATION.

DISPOSAL CONSIDERATIONS

CATALYSTS AND EXPENSIVE METALS SHOULD BE RECOVERED FOR REUSE
OR RECYCLING.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

REGULATORY INFORMATION

REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY

10. Propadiene

CHEMICAL IDENTIFICATION

CATALOG #: 294985
NAME: ALLENE, 97%

COMPOSITION/INFORMATION ON INGREDIENTS

CAS #: 463-49-0
MF: C3H4
EC NO: 207-335-3

HAZARDS IDENTIFICATION

LABEL PRECAUTIONARY STATEMENTS
FLAMMABLE (USA)
HIGHLY FLAMMABLE (EU)
DANGER: FLAMMABLE HIGH-PRESSURE GAS.
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
TAKE PRECAUTIONARY MEASURES AGAINST STATIC DISCHARGES.
IN CASE OF INSUFFICIENT VENTILATION, WEAR SUITABLE RESPIRATORY EQUIPMENT.
CYLINDER TEMPERATURE SHOULD NOT EXCEED 125 F(52 C).
DO NOT PUNCTURE OR INCINERATE THIS CYLINDER.

FIRST-AID MEASURES

IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES WITH COPIOUS AMOUNTS OF WATER FOR AT LEAST 15 MINUTES.
IN CASE OF CONTACT, IMMEDIATELY WASH SKIN WITH SOAP AND COPIOUS AMOUNTS OF WATER.
IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
CALL A PHYSICIAN.

FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA
USE WATER SPRAY OR FOG NOZZLE TO KEEP CYLINDER COOL. MOVE CYLINDER AWAY FROM FIRE IF THERE IS NO RISK.
SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.
DANGER: FLAMMABLE HIGH-PRESSURE GAS.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
VAPOR MAY TRAVEL CONSIDERABLE DISTANCE TO SOURCE OF IGNITION AND FLASH BACK.
CONTAINER EXPLOSION MAY OCCUR UNDER FIRE CONDITIONS.
MAY FORM EXPLOSIVE MIXTURES WITH AIR.

ACCIDENTAL RELEASE MEASURES

EVACUATE AREA AND KEEP PERSONNEL UPWIND.
SHUT OFF ALL SOURCES OF IGNITION.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
SHUT OFF LEAK IF THERE IS NO RISK.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

HANDLING AND STORAGE

REFER TO NEXT SECTION.

ADDITIONAL INFORMATION

ALLENE CAN DECOMPOSE EXPLOSIVELY UNDER A PRESSURE OF 2 BAR.
INCOMPATIBLE WITH COPPER, SILVER, MERCURY AND THEIR ALLOYS.

EXPOSURE CONTROLS/PERSONAL PROTECTION

CHEMICAL SAFETY GOGGLES.
COMPATIBLE CHEMICAL-RESISTANT GLOVES.
NIOSH/MSHA-APPROVED RESPIRATOR.
SAFETY SHOWER AND EYE BATH.
MECHANICAL EXHAUST REQUIRED.
DO NOT BREATHE GAS.
DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
WASH THOROUGHLY AFTER HANDLING.
KEEP TIGHTLY CLOSED.
KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.
CYLINDER TEMPERATURE SHOULD NOT EXCEED 125 F(52 C).
STORE AND USE WITH ADEQUATE VENTILATION.
CONTENTS UNDER PRESSURE.
WARNING: SUCK-BACK INTO CYLINDER MAY CAUSE RUPTURE.
USE BACK-FLOW-PREVENTIVE DEVICE IN PIPING.
USE WITH EQUIPMENT RATED FOR CYLINDER PRESSURE, AND OF COMPATIBLE MATERIALS OF CONSTRUCTION. CLOSE VALVE WHEN NOT IN USE AND WHEN EMPTY.
MAKE SURE CYLINDER IS PROPERLY SECURED WHEN IN USE OR STORED.

PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AND ODOR

COLORLESS GAS

PHYSICAL PROPERTIES

BOILING POINT: -34 C
MELTING POINT: -136 C
EXPLOSION LIMITS IN AIR:
UPPER 13%
LOWER 2.1%
VAPOR PRESSURE: 6795MM 21 C 8687MM 37.7 C
VAPOR DENSITY: 1.42 @ 20 C

STABILITY AND REACTIVITY

INCOMPATIBILITIES

STRONG OXIDIZING AGENTS
STRONG BASES

HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS

CARBON MONOXIDE, CARBON DIOXIDE

TOXICOLOGICAL INFORMATION

ACUTE EFFECTS

MAY BE HARMFUL IF INHALED.

DISPOSAL CONSIDERATIONS

CAUTION: NO-RETURN CYLINDER. DO NOT REUSE. EMPTY CYLINDER WILL CONTAIN HAZARDOUS RESIDUE. FOLLOW PROPER DISPOSAL TECHNIQUES.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

REGULATORY INFORMATION

EUROPEAN INFORMATION

HIGHLY FLAMMABLE
HIGHLY FLAMMABLE
S 16
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
S 33
TAKE PRECAUTIONARY MEASURES AGAINST STATIC DISCHARGES.
S 38
IN CASE OF INSUFFICIENT VENTILATION, WEAR SUITABLE
RESPIRATORY EQUIPMENT.

11. Propane

CHEMICAL IDENTIFICATION

CATALOG #: 295655
NAME: PROPANE, 98%

COMPOSITION/INFORMATION ON INGREDIENTS

CAS #: 74-98-6
MF: C3H8
EC NO: 200-827-9
SYNONYMS
DIMETHYLMETHANE * LIQUEFIED PETROLEUM GAS * LPG * PROPANE (ACGIH:OSHA) * N-PROPANE * PROPYL HYDRIDE * R 290 *

HAZARDS IDENTIFICATION

LABEL PRECAUTIONARY STATEMENTS
FLAMMABLE (USA)
HIGHLY FLAMMABLE (EU)
EXTREMELY FLAMMABLE LIQUEFIED GAS.
DANGER: FLAMMABLE HIGH-PRESSURE LIQUID AND GAS.
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
TAKE PRECAUTIONARY MEASURES AGAINST STATIC DISCHARGES.
IN CASE OF INSUFFICIENT VENTILATION, WEAR SUITABLE RESPIRATORY EQUIPMENT.
WEAR SUITABLE PROTECTIVE CLOTHING.
CYLINDER TEMPERATURE SHOULD NOT EXCEED 125 F(52 C).
DO NOT PUNCTURE OR INCINERATE THIS CYLINDER.

FIRST-AID MEASURES

IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS. CALL A PHYSICIAN.

FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA
DO NOT EXTINGUISH BURNING GAS IF FLOW CANNOT BE SHUT OFF IMMEDIATELY. USE WATER SPRAY OR FOG NOZZLE TO KEEP CYLINDER COOL. MOVE CYLINDER AWAY FROM FIRE IF THERE IS NO RISK.
SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO PREVENT CONTACT WITH SKIN AND EYES.
DANGER: FLAMMABLE HIGH-PRESSURE LIQUID AND GAS.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
MAY FORM EXPLOSIVE MIXTURES WITH AIR.
VAPOR MAY TRAVEL CONSIDERABLE DISTANCE TO SOURCE OF IGNITION AND FLASH BACK.

ACCIDENTAL RELEASE MEASURES

EVACUATE AREA AND KEEP PERSONNEL UPWIND.
SHUT OFF ALL SOURCES OF IGNITION.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.

SHUT OFF LEAK IF THERE IS NO RISK.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

HANDLING AND STORAGE

REFER TO NEXT SECTION.

ADDITIONAL INFORMATION

HEATING BARIUM PEROXIDE UNDER GASEOUS PROPANE AT AMBIENT PRESSURE RESULTED IN A VIOLENT EXOTHERMIC REACTION. REACTS EXPLOSIVELY WITH CHLORINE DIOXIDE.

EXPOSURE CONTROLS/PERSONAL PROTECTION

CHEMICAL SAFETY GOGGLES.
COMPATIBLE CHEMICAL-RESISTANT GLOVES.
MECHANICAL EXHAUST REQUIRED.
NIOSH/MSHA-APPROVED RESPIRATOR IN NONVENTILATED AREAS AND/OR FOR EXPOSURE ABOVE THE ACGIH TLV.
DO NOT BREATHE GAS.
DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
WASH THOROUGHLY AFTER HANDLING.
KEEP TIGHTLY CLOSED.
KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.
CYLINDER TEMPERATURE SHOULD NOT EXCEED 125 F(52 C).
STORE AND USE WITH ADEQUATE VENTILATION.
CONTENTS UNDER PRESSURE.
WARNING: SUCK-BACK INTO CYLINDER MAY CAUSE RUPTURE.
USE BACK-FLOW-PREVENTIVE DEVICE IN PIPING.
USE WITH EQUIPMENT RATED FOR CYLINDER PRESSURE, AND OF COMPATIBLE MATERIALS OF CONSTRUCTION. CLOSE VALVE WHEN NOT IN USE AND WHEN EMPTY.
MAKE SURE CYLINDER IS PROPERLY SECURED WHEN IN USE OR STORED.

PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AND ODOR

COLORLESS GAS

PHYSICAL PROPERTIES

BOILING POINT: -42.1 C
MELTING POINT: -188 C
EXPLOSION LIMITS IN AIR:
UPPER 9.5%
LOWER 2.1%
AUTOIGNITION TEMPERATURE: 842 F 449C
VAPOR PRESSURE: 8.42ATM 21.1 C 190PSI 37.7 C
VAPOR DENSITY: 1.5

STABILITY AND REACTIVITY

INCOMPATIBILITIES

STRONG OXIDIZING AGENTS

HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS

CARBON MONOXIDE, CARBON DIOXIDE

TOXICOLOGICAL INFORMATION

ACUTE EFFECTS

MAY BE HARMFUL IF INHALED.
CAN CAUSE RAPID SUFFOCATION.

ADDITIONAL INFORMATION

INHALATION OF PROPANE AT CONCENTRATIONS SUFFICENT TO EXCLUDE AN ADEQUATE SUPPLY OF OXYGEN TO THE LUNGS CAN RESULT IN DIZZINESS, DROWSINESS AND EVENTUAL UNCONSCIOUSNESS. IT HAS A NARCOTIC ACTION AND ACTS AS A DEPRESSANT ON THE CENTRAL NERVOUS SYSTEM.
RTECS #: TX2275000
PROPANE
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.

DISPOSAL CONSIDERATIONS

CAUTION: NO-RETURN CYLINDER. DO NOT REUSE. EMPTY CYLINDER WILL CONTAIN HAZARDOUS RESIDUE. FOLLOW PROPER DISPOSAL TECHNIQUES.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

REGULATORY INFORMATION

EUROPEAN INFORMATION
EC INDEX NO: 601-003-00-5
HIGHLY FLAMMABLE
R 12
EXTREMELY FLAMMABLE.
S 9
KEEP CONTAINER IN A WELL-VENTILATED PLACE.
S 16
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
ACGIH TLV-SIMPLE ASPHYXIANT, NO TWA DTLVS* TLV/BEI,1997
MSHA STANDARD:ASPHYXIANTS/GASES
DTLWS* 3,215,1973
OSHA PEL (GEN INDU):8H TWA 1000 PPM (1800 MG/M3)
CFRGBR 29,1910.1000,1994
OSHA PEL (FED CONT):8H TWA 1000 PPM (1800 MG/M3)
CFRGBR 41,50-204.50,1994
NIOSH REL TO PROPANE-AIR:10H TWA 1000 PPM
NIOSH* DHHS #92-100,1992
NOHS 1974: HZD 26615; NIS 342; TNF 95086; NOS 192; TNE 1005020
NOES 1983: HZD 26615; NIS 396; TNF 129448; NOS 236; TNE 2071479; TFE 528348
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY
EPA TSCA SECTION 8(D) UNPUBLISHED HEALTH/SAFETY STUDIES
EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JUNE 1998

12. Propylene

CHEMICAL IDENTIFICATION

CATALOG #: 295663
NAME: PROPENE, 99+%

COMPOSITION/INFORMATION ON INGREDIENTS

CAS #: 115-07-1
MF: C3H6
EC NO: 204-062-1
SYNONYMS
METHYLETHENE * METHYLETHYLENE * NCI-C50077 * 1-PROPENE (9CI) *
PROPYLENE * 1-PROPYLENE * PROPYLENE (ACGIH) * R 1270 *

HAZARDS IDENTIFICATION

LABEL PRECAUTIONARY STATEMENTS
FLAMMABLE (USA)
HIGHLY FLAMMABLE (EU)
EXTREMELY FLAMMABLE LIQUEFIED GAS.
DANGER: FLAMMABLE HIGH-PRESSURE LIQUID AND GAS.
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
TAKE PRECAUTIONARY MEASURES AGAINST STATIC DISCHARGES.
IN CASE OF INSUFFICIENT VENTILATION, WEAR SUITABLE
RESPIRATORY EQUIPMENT.
CYLINDER TEMPERATURE SHOULD NOT EXCEED 125 F(52 C).
DO NOT PUNCTURE OR INCINERATE THIS CYLINDER.

FIRST-AID MEASURES

IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL
RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.
IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
CALL A PHYSICIAN.

FIRE FIGHTING MEASURES

EXTINGUISHING MEDIA
DO NOT EXTINGUISH BURNING GAS IF FLOW CANNOT BE SHUT OFF IMMEDIATELY.
USE WATER SPRAY OR FOG NOZZLE TO KEEP CYLINDER COOL. MOVE CYLINDER
AWAY FROM FIRE IF THERE IS NO RISK.
SPECIAL FIREFIGHTING PROCEDURES
WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO
PREVENT CONTACT WITH SKIN AND EYES.
DANGER: FLAMMABLE HIGH-PRESSURE LIQUID AND GAS.
UNUSUAL FIRE AND EXPLOSIONS HAZARDS
MAY FORM EXPLOSIVE MIXTURES WITH AIR.
VAPOR MAY TRAVEL CONSIDERABLE DISTANCE TO SOURCE OF IGNITION AND
FLASH BACK.

ACCIDENTAL RELEASE MEASURES

EVACUATE AREA AND KEEP PERSONNEL UPWIND.
SHUT OFF ALL SOURCES OF IGNITION.
WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY
RUBBER GLOVES.
SHUT OFF LEAK IF THERE IS NO RISK.
VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

HANDLING AND STORAGE

REFER TO NEXT SECTION.

ADDITIONAL INFORMATION

INCOMPATIBLE WITH SULFUR DIOXIDE, NITROGEN OXIDE, TRIFLUOROMETHYL HYPOFLUORITE.

EXPOSURE CONTROLS/PERSONAL PROTECTION

CHEMICAL SAFETY GOGGLES.
COMPATIBLE CHEMICAL-RESISTANT GLOVES.
MECHANICAL EXHAUST REQUIRED.
NIOSH/MSHA-APPROVED RESPIRATOR IN NONVENTILATED AREAS AND/OR FOR EXPOSURE ABOVE THE ACGIH TLV.
DO NOT BREATHE GAS.
DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
AVOID PROLONGED OR REPEATED EXPOSURE.
WASH THOROUGHLY AFTER HANDLING.
KEEP TIGHTLY CLOSED.
KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.
CYLINDER TEMPERATURE SHOULD NOT EXCEED 125 F(52 C).
STORE AND USE WITH ADEQUATE VENTILATION.
CONTENTS UNDER PRESSURE.
WARNING: SUCK-BACK INTO CYLINDER MAY CAUSE RUPTURE.
USE BACK-FLOW-PREVENTIVE DEVICE IN PIPING.
USE WITH EQUIPMENT RATED FOR CYLINDER PRESSURE, AND OF COMPATIBLE MATERIALS OF CONSTRUCTION. CLOSE VALVE WHEN NOT IN USE AND WHEN EMPTY.
MAKE SURE CYLINDER IS PROPERLY SECURED WHEN IN USE OR STORED.

PHYSICAL AND CHEMICAL PROPERTIES

APPEARANCE AND ODOR

COLORLESS GAS

PHYSICAL PROPERTIES

BOILING POINT: -47.7 C
MELTING POINT: -185 C
EXPLOSION LIMITS IN AIR:
UPPER 11.1%
LOWER 2%
AUTOIGNITION TEMPERATURE: 860 F 459C
VAPOR PRESSURE: 15.4ATM 37.7 C
VAPOR DENSITY: 1.48

STABILITY AND REACTIVITY

INCOMPATIBILITIES

STRONG OXIDIZING AGENTS
STRONG ACIDS

HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS

CARBON MONOXIDE, CARBON DIOXIDE

TOXICOLOGICAL INFORMATION

ACUTE EFFECTS

MAY BE HARMFUL.

ADDITIONAL INFORMATION

ACTS AS A SIMPLE ASPHYXIANT. SYMPTOMS OF OVEREXPOSURE INCLUDE DIZZINESS, DISORIENTATION, HEADACHE, EXCITATION, CENTRAL NERVOUS SYSTEM DEPRESSION AND ANESTHESIA.

RTECS #: UC6740000
PROPENE
ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR COMPLETE INFORMATION.

DISPOSAL CONSIDERATIONS

CAUTION: NO-RETURN CYLINDER. DO NOT REUSE. EMPTY CYLINDER WILL CONTAIN HAZARDOUS RESIDUE. FOLLOW PROPER DISPOSAL TECHNIQUES.
OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

REGULATORY INFORMATION

EUROPEAN INFORMATION
EC INDEX NO: 601-011-00-9
HIGHLY FLAMMABLE
R 12
EXTREMELY FLAMMABLE.
S 9
KEEP CONTAINER IN A WELL-VENTILATED PLACE.
S 16
KEEP AWAY FROM SOURCES OF IGNITION - NO SMOKING.
S 33
TAKE PRECAUTIONARY MEASURES AGAINST STATIC DISCHARGES.
REVIEWS, STANDARDS, AND REGULATIONS
OEL=MAK
ACGIH TLV-NOT CLASSIFIABLE AS A HUMAN CARCINOGEN DTLVS* TLV/BEI,1997
ACGIH TLV-SIMPLE ASPHYXIANT, NO TWA DTLVS* TLV/BEI,1997
IARC CANCER REVIEW:HUMAN NO ADEQUATE DATA IMEMDT 19,213,1979
IARC CANCER REVIEW:ANIMAL NO ADEQUATE DATA IMEMDT 19,213,1979
IARC CANCER REVIEW:ANIMAL INADEQUATE EVIDENCE IMEMDT 60,161,1994
IARC CANCER REVIEW:HUMAN INADEQUATE EVIDENCE IMEMDT 60,161,1994
IARC CANCER REVIEW:GROUP 3 IMEMDT 60,161,1994
NOHS 1974: HZD 63495; NIS 16; TNF 493; NOS 32; TNE 7150
NOES 1983: HZD 63495; NIS 7; TNF 162; NOS 25; TNE 7305; TFE 975
EPA TSCA SECTION 8(B) CHEMICAL INVENTORY
EPA TSCA SECTION 8(D) UNPUBLISHED HEALTH/SAFETY STUDIES
EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JUNE 1998
NTP CARCINOGENESIS STUDIES (INHALATION);NO EVIDENCE:MOUSE,RAT
NTPTR* NTP-TR-272,85
U.S. INFORMATION
THIS PRODUCT IS SUBJECT TO SARA SECTION 313 REPORTING REQUIREMENTS.

13. Water

WE ARE NOT AWARE OF ANY HAZARDS FOR THE ABOVE PRODUCT.

E. ASPEN® Report

OVERALL FLOWSHEET BALANCE

	*** MASS AND ENERGY BALANCE *** IN	OUT	GENERATION	RELATIVE DIFF.
CONVENTIONAL COMPONENTS (LBMOL/HR)				
CO	157.000	24.02	-133.	0.536E-08
PROPYLENE	1.50	1.50	0.0	-0.120E-10
PROPANE	146.	146.	0.0	-0.189E-08
PD	73.9	14.8	-59.1	-0.787E-07
MA	73.9	0.000486	-73.8745	0.124E-11
MEOH	140.	7.38	-133.	0.159E-04
MMA	0.0	131.	131.	-0.124E-04
MC	0.0	1.99	1.99	0.753E-05
ACID	0.745	0.745	0.0	-0.169E-07
WATER	2760.	760.	0.0	0.0
P-MET-01	0.0129	0.0129	0.0	-0.000355
TOTAL BALANCE				
MOLE(LBMOL/HR)	3360.	3090.	-266.	0.181E-06
MASS(LB/HR)	71,200.	71,200.		-0.135E-05
ENTHALPY(BTU/HR)	-358,000,000	-368,000,000		0.0267

BLOCK: B590 MODEL: COMPR

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INLET STREAM:                550
OUTLET STREAM:               590
PROPERTY OPTION SET:         UNIQUAC   UNIQUAC / IDEAL GAS

                      ***  MASS AND ENERGY BALANCE  ***
                                   IN                OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)                319.853           319.853          0.0
    MASS(LB/HR)                   21570.3           21570.3       -0.168657E-15
    ENTHALPY(BTU/HR)           -0.369150E+08     -0.364917E+08    -0.0114660

                          ***  INPUT DATA  ***

ISENTROPIC CENTRIFUGAL COMPRESSOR
 OUTLET PRESSURE  PSI                                              34.2000
 ISENTROPIC EFFICIENCY                                             0.72000
 MECHANICAL EFFICIENCY                                             1.00000

                          ***  RESULTS  ***

 INDICATED  HORSEPOWER REQUIREMENT  HP                            166.
 BRAKE      HORSEPOWER REQUIREMENT  HP                            166.
 NET WORK, HP                                                    -166.
 ISENTROPIC HORSEPOWER REQUIREMENT  HP                            119.
 CALCULATED OUTLET TEMP  F                                        251.
 ISENTROPIC TEMPERATURE  F                                        235.
 EFFICIENCY (POLYTR/ISENTR) USED                                    0.72
 OUTLET VAPOR FRACTION                                              1.00
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BLOCK: D250 MODEL: RADFRAC

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  INLETS   - 190        STAGE  97
             250        STAGE   2
  OUTLETS  - 299        STAGE   1
             280        STAGE   1
             275        STAGE 150
 PROPERTY OPTION SET:   UNIQUAC   UNIQUAC / IDEAL GAS

                    ***  MASS AND ENERGY BALANCE  ***
                                 IN                  OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)              591.766             591.766        -0.384229E-15
    MASS(LB/HR    )             24283.0             24283.0         0.658142E-12
    ENTHALPY(BTU/HR  )      -0.290687E+08       -0.264763E+08       -0.0891812

                          ************************
                          ****  INPUT DATA  ****
                          ************************

****    INPUT PARAMETERS    ****

 NUMBER OF STAGES                                                    150
 ALGORITHM OPTION                                                  STANDARD
 ABSORBER OPTION                                                   NO
 INITIALIZATION OPTION                                             STANDARD
 HYDRAULIC PARAMETER CALCULATIONS                                  NO
 INSIDE LOOP CONVERGENCE METHOD                                    BROYDEN
 DESIGN SPECIFICATION METHOD                                       NESTED
 MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS                             30
 MAXIMUM NO. OF INSIDE LOOP ITERATIONS                              10
 MAXIMUM NUMBER OF FLASH ITERATIONS                                 50
 FLASH TOLERANCE                                                    0.00010000
 OUTSIDE LOOP CONVERGENCE TOLERANCE                                 0.00010000

****    COL-SPECS    ****

 MOLAR VAPOR DIST / TOTAL DIST                                      0.010000
 MOLAR REFLUX RATIO                                                 7.04200
 MOLAR DISTILLATE RATE              LBMOL/HR                      168.276

****     PROFILES    ****

 P-SPEC          STAGE   1  PRES, PSI                             257.000

**** TRAY MURPHREE EFFICIENCY ****

                    STAGE    1  EFFICIENCY                        1.0000
                             2                                   0.70000
                           149                                   0.70000
                           150                                    1.0000
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                          ********************
                          ****  RESULTS  ****
                          ********************

***   COMPONENT SPLIT FRACTIONS   ***

                                OUTLET STREAMS
                                --------------
                    299           280           275
 COMPONENT:
 CO              0.33975       0.66025       0.0
 PROPYLEN        0.011449      0.98855       0.48276E-11
 PROPANE         0.0094612     0.99027       0.00027132
 PD              0.0066761     0.83409       0.15924
 MA              0.22987E-07   0.36312E-05   1.0000
 MEOH            0.13336E-05   0.0047372     0.99526
 MMA             0.11771E-06   0.0014837     0.99852
 MC              0.32176E-07   0.0006962     0.99930
 ACID            0.11353E-16   0.18674E-07   1.0000
 P-MET-01        0.34210E-13   0.95764E-06   1.0000


***    SUMMARY OF KEY RESULTS    ***

 TOP STAGE TEMPERATURE              F                      120.117
 BOTTOM STAGE TEMPERATURE           F                      250.828
 TOP STAGE LIQUID FLOW              LBMOL/HR             1,147.61
 BOTTOM STAGE LIQUID FLOW           LBMOL/HR               428.799
 TOP STAGE VAPOR FLOW               LBMOL/HR                 1.62967
 BOTTOM STAGE VAPOR FLOW            LBMOL/HR             1,109.40
 MOLAR REFLUX RATIO                                        7.04200
 MOLAR BOILUP RATIO                                        2.58722
 CONDENSER DUTY (W/O SUBCOOL)       BTU/HR          -7,870,510.
 REBOILER DUTY                      BTU/HR          10,462,900.


   ****   MANIPULATED VARIABLES   ****

                                                    BOUNDS
CALCULATED
                                              LOWER          UPPER          VALUE
   MOLAR DISTILLATE RATE       LBMOL/HR       1.0000         1000.0         162.97


   ****    DESIGN SPECIFICATIONS   ****

 NO  SPEC-TYPE     QUALIFIERS                  UNIT       SPECIFIED
CALCULATED
                                                          VALUE          VALUE
  1  MOLE-FRAC     STREAMS: 275                           0.0190         0.0190
                   COMPS:   PD
                   BASE-COMPS:   PD
                                 MA
```

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****   MAXIMUM FINAL RELATIVE ERRORS   ****

  DEW POINT                      0.55946E-05  STAGE= 29
  BUBBLE POINT                   0.25172E-05  STAGE= 31
  COMPONENT MASS BALANCE         0.15584E-05  STAGE=144 COMP=MC
  ENERGY BALANCE                 0.17619E-05  STAGE=145

   ****    PROFILES   ****

   **NOTE** REPORTED VALUES FOR STAGE LIQUID AND VAPOR RATES ARE THE FLOWS
            FROM THE STAGE EXCLUDING ANY SIDE PRODUCT.  FOR THE FIRST STAGE,
            THE REPORTED VAPOR FLOW IS THE VAPOR DISTILLATE FLOW.  FOR THE
            LAST STAGE, THE REPORTED LIQUID FLOW IS THE LIQUID BOTTOMS FLOW.

                                                ENTHALPY
STAGE TEMPERATURE    PRESSURE                   BTU/LBMOL          HEAT DUTY
      F              PSI                 LIQUID        VAPOR       BTU/HR
    1   120.12       257.00             -39090.       -35492.    -.78705+07
    2   142.30       257.10             -49260.       -33080.
    3   142.67       257.20             -48364.       -32153.
    4   142.88       257.30             -47458.       -31199.
    5   143.08       257.40             -46528.       -30209.
   96   160.27       266.50              1365.2        22993.
   97   156.94       266.60              6151.3        24018.
   98   157.65       266.70              8521.5        27085.
  149   196.70       271.80               10264.       63366.
  150   250.83       271.90             -46903.       41791.     .10463+08

STAGE      FLOW RATE                          FEED RATE                PRODUCT RATE
             LBMOL/HR                          LBMOL/HR                  LBMOL/HR
        LIQUID       VAPOR          LIQUID     VAPOR     MIXED      LIQUID     VAPOR
    1   1148.        1.630                                          161.3372   1.6296
    2   1722.        1311.        296.2660
    3   1724.        1589.
   96   1631.        1483.
   97   2015.        1498.        295.5000
   98   2009.        1587.
  149   1538.        1302.
  150   428.8        1109.                                          428.7990

   ****  MASS FLOW PROFILES  ****

STAGE      FLOW RATE                          FEED RATE                PRODUCT RATE
             LB/HR                             LB/HR                     LB/HR
        LIQUID       VAPOR          LIQUID     VAPOR     MIXED      LIQUID     VAPOR
    1 0.5009E+05     69.45                                          7041.2864  69.4541
    2 0.7408E+05 0.5720E+05       .11851+05
    3 0.7410E+05 0.6934E+05
    4 0.7402E+05 0.6936E+05
    5 0.7393E+05 0.6928E+05
   96 0.6737E+05 0.6205E+05
   97 0.8336E+05 0.6263E+05       .12432+05
   98 0.8292E+05 0.6618E+05
  149 0.6054E+05 0.5152E+05
  150 0.1717E+05 0.4337E+05                                          .17172+05
```

**** MOLE-X-PROFILE ****

STAGE	CO	PROPYLEN	PROPANE	PD	MA
1	0.0014488	0.0091792	0.89780	0.083615	0.29929E-05
2	0.000038439	0.0056412	0.73916	0.077545	0.31691E-05
3	0.10390E-05	0.0042819	0.73317	0.085059	0.39761E-05
4	0.28049E-07	0.0033435	0.72642	0.092641	0.49201E-05
5	0.75646E-09	0.0026973	0.71929	0.10030	0.60239E-05
96	0.0	0.00095892	0.31995	0.15609	0.33475
97	0.0	0.0011552	0.33199	0.14778	0.36616
98	0.0	0.00082357	0.31223	0.15354	0.37987
149	0.0	0.11407E-12	0.00022038	0.012775	0.62509
150	0.0	0.16866E-13	0.000092552	0.0060062	0.31011

**** MOLE-X-PROFILE ****

STAGE	MEOH	MMA	MC	ACID	P-MET-01
1	0.0076342	0.00031566	0.71386E-06	0.72066E-14	0.70165E-11
2	0.15732	0.020194	0.000096650	0.36152E-07	0.68638E-06
3	0.15721	0.020176	0.000096562	0.36117E-07	0.68573E-06
4	0.15731	0.020186	0.000096604	0.36132E-07	0.68601E-06
5	0.15741	0.020196	0.000096653	0.36150E-07	0.68634E-06
96	0.16682	0.021323	0.00010207	0.38171E-07	0.72472E-06
97	0.13555	0.017277	0.000082653	0.30894E-07	0.58655E-06
98	0.13611	0.017338	0.000082935	0.30996E-07	0.58850E-06
149	0.32968	0.032121	0.00011842	0.40479E-07	0.76932E-06
150	0.60347	0.079932	0.00038553	0.14520E-06	0.27568E-05

**** MOLE-Y-PROFILE ****

STAGE	CO	PROPYLEN	PROPANE	PD	MA
1	0.073803	0.010525	0.84920	0.066257	0.18756E-05
2	0.0015387	0.0091809	0.89774	0.083594	0.29915E-05
3	0.000041663	0.0070573	0.89318	0.091728	0.37408E-05
4	0.11261E-05	0.0055827	0.88654	0.099857	0.46148E-05
5	0.30401E-07	0.0045661	0.87929	0.10808	0.56382E-05
96	0.0	0.0020525	0.45214	0.18718	0.34733
97	0.0	0.0020444	0.44604	0.17813	0.36454
98	0.0	0.0014674	0.42169	0.18610	0.38131
149	0.0	0.35116E-12	0.00038378	0.019971	0.87368
150	0.0	0.15165E-12	0.00026979	0.015391	0.74683

**** MOLE-Y-PROFILE ****

STAGE	MEOH	MMA	MC	ACID	P-MET-01
1	0.00021277	0.24793E-05	0.32663E-08	0.0	0.0
2	0.0076250	0.00031527	0.71298E-06	0.71977E-14	0.70078E-11
3	0.0076672	0.00031706	0.71718E-06	0.73134E-14	0.71049E-11
4	0.0077004	0.00031836	0.72007E-06	0.73919E-14	0.71696E-11
5	0.0077351	0.00031962	0.72277E-06	0.74675E-14	0.72314E-11
96	0.010882	0.00042359	0.94837E-06	0.16232E-13	0.13441E-10
97	0.0089061	0.00033763	0.78205E-06	0.12488E-13	0.10481E-10
98	0.0090847	0.00034340	0.79447E-06	0.12967E-13	0.10804E-10
149	0.10072	0.0052438	0.60791E-05	0.93434E-12	0.38135E-09
150	0.22385	0.013641	0.000015184	0.28871E-11	0.11343E-08

**** K-VALUES ****

STAGE	CO	PROPYLEN	PROPANE	PD	MA
1	50.942	1.1466	0.94586	0.79240	0.62669
2	56.722	1.7888	1.2172	1.0330	0.84261
3	56.822	1.7957	1.2221	1.0375	0.84662
4	56.886	1.8000	1.2247	1.0398	0.84880
5	56.948	1.8040	1.2270	1.0421	0.85083
96	60.631	2.1440	1.4213	1.2240	1.0155
97	59.766	1.9839	1.3750	1.1822	0.97595
98	60.003	2.0005	1.3845	1.1912	0.98404
149	69.587	3.8280	1.9631	1.7169	1.4846
150	79.230	8.9911	2.9150	2.5626	2.4083

**** K-VALUES ****

STAGE	MEOH	MMA	MC	ACID	P-MET-01
1	0.027870	0.0078544	0.0045755	0.60191E-07	0.35367E-05
2	0.048351	0.015575	0.0073582	0.19773E-06	0.000010149
3	0.048679	0.015687	0.0074144	0.20156E-06	0.000010321
4	0.048857	0.015745	0.0074418	0.20368E-06	0.000010413
5	0.049041	0.015799	0.0074665	0.20569E-06	0.00010498
96	0.070305	0.021593	0.0099898	0.46729E-06	0.000020297
97	0.065139	0.019399	0.0093974	0.39758E-06	0.000017631
98	0.066160	0.019659	0.0095135	0.41141E-06	0.000018114
149	0.14544	0.051211	0.018384	0.24076E-05	0.000076237
150	0.37094	0.17066	0.039384	0.000019883	0.00041146

**** MASS-X-PROFILE ****

STAGE	CO	PROPYLEN	PROPANE	PD	MA
1	0.00092981	0.0088505	0.90713	0.076759	0.27475E-05
2	0.000025032	0.0055190	0.75779	0.072231	0.29520E-05
3	0.67703E-06	0.0041918	0.75212	0.079279	0.37059E-05
4	0.18290E-07	0.0032754	0.74570	0.086405	0.45889E-05
5	0.49361E-09	0.0026442	0.73890	0.093616	0.56224E-05
96	0.0	0.00097693	0.34158	0.15140	0.32470
97	0.0	0.0011753	0.35395	0.14315	0.35469
98	0.0	0.00083955	0.33354	0.14902	0.36870
149	0.0	0.12197E-12	0.00024692	0.013005	0.63633
150	0.0	0.17723E-13	0.00010191	0.0060088	0.31024

**** MASS-X-PROFILE ****

STAGE	MEOH	MMA	MC	ACID	P-MET-01
1	0.0056049	0.00072413	0.16376E-05	0.16195E-13	0.19958E-10
2	0.11720	0.047004	0.00022497	0.82435E-07	0.19810E-05
3	0.11719	0.046992	0.00022491	0.82408E-07	0.19803E-05
4	0.11734	0.047046	0.00022516	0.82498E-07	0.19825E-05
5	0.11750	0.047104	0.00022543	0.82597E-07	0.19849E-05
96	0.12941	0.051684	0.00024741	0.90637E-07	0.21781E-05
97	0.10501	0.041821	0.00020007	0.73259E-07	0.17605E-05
98	0.10566	0.042051	0.00020115	0.73646E-07	0.17698E-05
149	0.26840	0.081711	0.00030126	0.10088E-06	0.24266E-05
150	0.48284	0.19983	0.00096385	0.35561E-06	0.85455E-05

**** MASS-Y-PROFILE ****

STAGE	CO	PROPYLEN	PROPANE	PD	MA
1	0.048506	0.010392	0.87865	0.062287	0.17632E-05
2	0.00098758	0.0088524	0.90709	0.076742	0.27463E-05
3	0.000026744	0.0068056	0.90259	0.084219	0.34346E-05
4	0.72330E-06	0.0053872	0.89647	0.091744	0.42399E-05
5	0.19542E-07	0.0044094	0.88979	0.099372	0.51839E-05
96	0.0	0.0020648	0.47664	0.17928	0.33267
97	0.0	0.0020574	0.47037	0.17067	0.34927
98	0.0	0.0014802	0.44576	0.17874	0.36622
149	0.0	0.37341E-12	0.00042765	0.020219	0.88452
150	0.0	0.16325E-12	0.00030434	0.015775	0.76545

**** MASS-Y-PROFILE ****

STAGE	MEOH	MMA	MC	ACID	P-MET-01
1	0.00015997	0.58243E-05	0.76732E-08	0.0	0.0
2	0.0055983	0.00072326	0.16357E-05	0.16176E-13	0.19934E-10
3	0.0056299	0.00072743	0.16455E-05	0.16438E-13	0.20212E-10
4	0.0056581	0.00073092	0.16532E-05	0.16625E-13	0.20410E-10
5	0.0056877	0.00073432	0.16606E-05	0.16808E-13	0.20601E-10
96	0.0083355	0.0010138	0.22699E-05	0.38060E-13	0.39889E-10
97	0.0068244	0.00080837	0.18724E-05	0.29291E-13	0.31114E-10
98	0.0069780	0.00082415	0.19068E-05	0.30488E-13	0.32152E-10
149	0.081551	0.013266	0.000015380	0.23157E-11	0.11963E-08
150	0.18349	0.034938	0.000038890	0.72439E-11	0.36023E-08

****
***** HYDRAULIC PARAMETERS *****
****

*** DEFINITIONS ***

MARANGONI INDEX = SIGMA - SIGMATO
FLOW PARAM = (ML/MV)*SQRT(RHOV/RHOL)
QR = QV*SQRT(RHOV/(RHOL-RHOV))
F FACTOR = QV*SQRT(RHOV)

WHERE:
SIGMA IS THE SURFACE TENSION OF LIQUID FROM THE STAGE
SIGMATO IS THE SURFACE TENSION OF LIQUID TO THE STAGE
ML IS THE MASS FLOW OF LIQUID FROM THE STAGE
MV IS THE MASS FLOW OF VAPOR TO THE STAGE
RHOL IS THE MASS DENSITY OF LIQUID FROM THE STAGE
RHOV IS THE MASS DENSITY OF VAPOR TO THE STAGE
QV IS THE VOLUMETRIC FLOW RATE OF VAPOR TO THE STAGE

	MASS FLOW LB/HR		VOLUME FLOW CUFT/HR		MOLECULAR WEIGHT	
STAGE	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO
1	57127.	57196.	1994.4	32930.	43.643	43.642
2	74077.	69337.	2438.1	39933.	43.012	43.637
3	74102.	69361.	2438.4	39973.	42.986	43.608
4	74021.	69280.	2434.0	39952.	42.956	43.576
5	73933.	69192.	2429.1	39929.	42.926	43.544
96	67374.	62634.	2077.7	37177.	41.305	41.816
97	83357.	66185.	2599.1	39410.	41.361	41.716
98	82918.	65746.	2576.3	39275.	41.279	41.614
149	60539.	43366.	1683.5	31110.	39.357	39.090
150	17172.	43366.	446.97	31110.	40.047	39.090

STAGE	DENSITY LB/CUFT LIQUID FROM	DENSITY LB/CUFT VAPOR TO	VISCOSITY CP LIQUID FROM	VISCOSITY CP VAPOR TO	SURFACE TENSION DYNE/CM LIQUID FROM
1	28.644	1.7369	0.077169	0.0092404	4.5019
2	30.383	1.7363	0.089214	0.0092354	6.0449
3	30.389	1.7352	0.089407	0.0092371	6.0386
4	30.412	1.7341	0.089744	0.0092390	6.0452
5	30.436	1.7329	0.090102	0.0092409	6.0528
96	32.428	1.6848	0.10663	0.0095946	7.0704
97	32.072	1.6794	0.10318	0.0096120	6.8227
98	32.185	1.6740	0.10431	0.0096300	6.8698
149	35.961	1.3940	0.13738	0.011659	8.6934
150	38.420	1.3940	0.15844	0.011659	9.5530

STAGE	MARANGONI INDEX DYNE/CM	FLOW PARAM	QR CUFT/HR	REDUCED F-FACTOR (LB-CUFT)**.5/HR
1		0.24595	8366.6	43399.
2	-1.8787	0.25540	9831.4	52620.
3	-0.0062687	0.25529	9836.7	52655.
4	0.66299	0.25513	9824.4	52611.
5	0.75627	0.25496	9810.9	52562.
96	0.25187	0.24519	8703.0	48255.
97	-.46588	0.28820	9264.0	51072.
98	0.047097	0.28762	9199.5	50815.
149	0.50215	0.27485	6247.3	36730.
150	0.85957	0.075427	6036.3	36730.

```
*****************************************
***** TRAY SIZING CALCULATIONS *****
*****************************************

*********************
*** SECTION   1 ***
*********************

STARTING STAGE NUMBER                                          2
ENDING STAGE NUMBER                                          149
FLOODING CALCULATION METHOD                                 FAIR

DESIGN PARAMETERS
-----------------
PEAK CAPACITY FACTOR                                     1.00000
SYSTEM FOAMING FACTOR                                    1.00000
FLOODING FACTOR                                          0.85000
MINIMUM COLUMN DIAMETER                  FT              1.00000
MINIMUM DC AREA/COLUMN AREA                              0.10000
HOLE AREA/ACTIVE AREA                                    0.12000

TRAY SPECIFICATIONS
-------------------
TRAY TYPE                                                  SIEVE
NUMBER OF PASSES                                               1
TRAY SPACING                             FT              1.66667
```

***** SIZING RESULTS @ STAGE WITH MAXIMUM DIAMETER *****

STAGE WITH MAXIMUM DIAMETER		3
COLUMN DIAMETER	FT	5.59079
DC AREA/COLUMN AREA		0.100000
DOWNCOMER VELOCITY	FT/SEC	0.27591
WEIR LENGTH	FT	4.06236

**** SIZING PROFILES ****

STAGE	DIAMETER FT	TOTAL AREA SQFT	ACTIVE AREA SQFT	SIDE DC AREA SQFT
2	5.5891	24.534	19.627	2.4534
3	5.5908	24.549	19.639	2.4549
4	5.5862	24.509	19.607	2.4509
96	5.1463	20.801	16.641	2.0801
97	5.4578	23.395	18.716	2.3395
98	5.4334	23.186	18.549	2.3186
148	4.6960	17.320	13.856	1.7320
149	4.3433	14.816	11.853	1.4816

BLOCK: D650 MODEL: RADFRAC

```
INLETS   - 590          STAGE   2
           815B         STAGE   1
  OUTLETS  - 699        STAGE   1
           655          STAGE   1
           675          STAGE  11
 PROPERTY OPTION SET:    UNIQUAC   UNIQUAC / IDEAL GAS

                    ***  MASS AND ENERGY BALANCE  ***
                                 IN                OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)            319.857           319.857            0.0
    MASS(LB/HR)               21570.9           21570.9        -0.760217E-11
    ENTHALPY(BTU/HR)       -0.364923E+08     -0.409451E+08      0.108750

                    ************************
                    ****  INPUT DATA  ****
                    ************************

****   INPUT PARAMETERS   ****

 NUMBER OF STAGES                                                  11
 ALGORITHM OPTION                                                  STANDARD
 ABSORBER OPTION                                                   NO
 INITIALIZATION OPTION                                             STANDARD
 HYDRAULIC PARAMETER CALCULATIONS                                  NO
 INSIDE LOOP CONVERGENCE METHOD                                    BROYDEN
 DESIGN SPECIFICATION METHOD                                       NESTED
 MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS                            100
 MAXIMUM NO. OF INSIDE LOOP ITERATIONS                             10
 MAXIMUM NUMBER OF FLASH ITERATIONS                                50
 FLASH TOLERANCE                                                    0.00010000
 OUTSIDE LOOP CONVERGENCE TOLERANCE                                 0.00010000

****   COL-SPECS   ****

 MOLAR VAPOR DIST / TOTAL DIST                                      0.17000
 MOLAR REFLUX RATIO                                                 3.00000
 DISTILLATE TO FEED RATIO                                           0.40000

****    PROFILES   ****

 P-SPEC          STAGE   1  PRES, PSI                              34.0000

**** TRAY MURPHREE EFFICIENCY ****

                    STAGE   1  EFFICIENCY                          1.0000
                            2                                     0.70000
                           10                                     0.70000
                           11                                      1.0000
```

```
                          ********************
                          ****  RESULTS  ****
                          ********************

***   COMPONENT SPLIT FRACTIONS   ***

                                OUTLET STREAMS
                                --------------
                    699             655             675
 COMPONENT:
 CO              0.98527         0.014735        0.16003E-24
 PROPANE         0.47671         0.52329         0.32347E-09
 PD              0.45691         0.54309         0.15891E-08
 MEOH            0.047815        0.95114         0.0010495
 MMA             0.0063602       0.20771         0.78593
 MC              0.00023748      0.076591        0.92317
 ACID            0.32077E-08     0.060539        0.93946
 P-MET-01        0.39195E-06     0.15021         0.84979


***    SUMMARY OF KEY RESULTS    ***

 TOP STAGE TEMPERATURE              F                      120.193
 BOTTOM STAGE TEMPERATURE           F                      269.160
 TOP STAGE LIQUID FLOW              LBMOL/HR               563.532
 BOTTOM STAGE LIQUID FLOW           LBMOL/HR               132.013
 TOP STAGE VAPOR FLOW               LBMOL/HR                31.9335
 BOTTOM STAGE VAPOR FLOW            LBMOL/HR               542.918
 MOLAR REFLUX RATIO                                          3.00000
 MOLAR BOILUP RATIO                                          4.11261
 CONDENSER DUTY (W/O SUBCOOL)       BTU/HR          -11,877,000.
 REBOILER DUTY                      BTU/HR            7,424,170.

 ****   MANIPULATED VARIABLES   ****

                                                  BOUNDS
CALCULATED
                                          LOWER          UPPER          VALUE
   DISTILLATE TO FEED RATIO               0.01000        0.90000        0.58727

 ****    DESIGN SPECIFICATIONS   ****

 NO  SPEC-TYPE     QUALIFIERS              UNIT       SPECIFIED
CALCULATED
                                                        VALUE          VALUE
 1  MOLE-FRAC     STREAMS: 675                          0.00100        0.00100
                  COMPS:   MEOH

 ****   MAXIMUM FINAL RELATIVE ERRORS   ****

  DEW POINT                          0.00024668   STAGE=  5
  BUBBLE POINT                       0.00030076   STAGE=  1
  COMPONENT MASS BALANCE             0.45871E-06  STAGE=  7 COMP=P-MET-01
  ENERGY BALANCE                     0.000028158  STAGE=  8
```

**** PROFILES ****

NOTE REPORTED VALUES FOR STAGE LIQUID AND VAPOR RATES ARE THE FLOWS FROM THE STAGE EXCLUDING ANY SIDE PRODUCT. FOR THE FIRST STAGE, THE REPORTED VAPOR FLOW IS THE VAPOR DISTILLATE FLOW. FOR THE LAST STAGE, THE REPORTED LIQUID FLOW IS THE LIQUID BOTTOMS FLOW.

STAGE	TEMPERATURE F	PRESSURE PSI	ENTHALPY BTU/LBMOL LIQUID	VAPOR	HEAT DUTY BTU/HR
1	120.19	34.000	-0.11464E+06	-53227.	-.11877+08
2	190.85	34.100	-0.12264E+06	-96226.	
3	193.59	34.200	-0.12314E+06	-96769.	
9	250.52	34.800	-0.16046E+06	-0.13651E+06	
10	265.14	34.900	-0.16171E+06	-0.14565E+06	
11	269.16	35.000	-0.16189E+06	-0.14799E+06	.74242+07

STAGE	FLOW RATE LBMOL/HR		FEED RATE LBMOL/HR			PRODUCT RATE LBMOL/HR	
	LIQUID	VAPOR	LIQUID	VAPOR	MIXED	LIQUID	VAPOR
1	563.5	31.93			0.0045156	155.9104	31.9334
2	619.1	751.4			319.8525		
3	622.8	487.1					
9	645.8	476.8					
10	674.9	513.7					
11	132.0	542.9				132.0131	

**** MASS FLOW PROFILES ****

STAGE	FLOW RATE LB/HR		FEED RATE LB/HR			PRODUCT RATE LB/HR	
	LIQUID	VAPOR	LIQUID	VAPOR	MIXED	LIQUID	VAPOR
1	0.2658E+05	1009.			0.5605	7353.8646	1009.0347
2	0.3484E+05	0.3494E+05			.21570+05		
3	0.3528E+05	0.2163E+05					
9	0.6297E+05	0.4135E+05					
10	0.6723E+05	0.4976E+05					
11	0.1321E+05	0.5402E+05				.13208+05	

**** MOLE-X-PROFILE ****

STAGE	CO	PROPANE	PD	MEOH	MMA
1	0.0022706	0.00013320	0.0089712	0.76739	0.22016
2	0.000092176	0.000020762	0.001514000	0.64262	0.35232
3	0.43490E-06	0.37999E-05	0.00030284	0.63821	0.35804
9	0.0	0.33001E-10	0.62811E-08	0.038262	0.95255
10	0.0	0.21809E-11	0.53552E-09	0.0074804	0.98157
11	0.0	0.97242E-13	0.31001E-10	0.0010001	0.98384

**** MOLE-X-PROFILE ****

STAGE	MC	ACID	P-MET-01
1	0.0010611	0.39934E-06	0.75819E-05
2	0.0034269	0.15605E-05	0.000010804
3	0.0034315	0.15514E-05	0.000010741
9	0.0091772	0.14971E-05	0.000010521
10	0.010934	0.14337E-05	0.000010300
11	0.015104	0.73189E-05	0.000050659

**** MOLE-Y-PROFILE ****

STAGE	CO	PROPANE	PD	MEOH	MMA
1	0.74127	0.00059245	0.036850	0.18835	0.032914
2	0.033678	0.00015272	0.010156	0.74279	0.21221
3	0.00011716	0.000026389	0.0019243	0.81649	0.18117
9	0.0	0.53890E-09	0.80534E-07	0.19660	0.79818
10	0.0	0.41456E-10	0.78871E-08	0.047837	0.94451
11	0.0	0.26875E-11	0.65820E-09	0.0090562	0.98102

**** MOLE-Y-PROFILE ****

STAGE	MC	ACID	P-MET-01
1	0.000016063	0.10331E-12	0.96592E-10
2	0.0010167	0.38237E-06	0.12499E-05
3	0.00026237	0.16079E-10	0.36108E-08
9	0.0052234	0.51302E-09	0.10027E-06
10	0.0076542	0.11080E-08	0.20701E-06
11	0.0099201	0.26538E-08	0.48637E-06

**** K-VALUES ****

STAGE	CO	PROPANE	PD	MEOH	MMA
1	326.33	4.4465	4.1065	0.24546	0.14947
2	383.18	9.1642	8.3504	1.2187	0.47826
3	384.16	9.3757	8.5323	1.2842	0.49587
9	424.43	22.789	17.778	6.8045	0.77210
10	444.53	26.628	20.513	8.6168	0.94630
11	448.90	27.637	21.231	9.0554	0.99714

**** K-VALUES ****

STAGE	MC	ACID	P-MET-01
1	0.015137	0.25880E-06	0.000012744
2	0.069253	0.88139E-05	0.00029119
3	0.072821	0.99334E-05	0.00032237
9	0.45565	0.00017222	0.0051792
10	0.61122	0.00031102	0.0084803
11	0.65677	0.00036259	0.0096008

**** MASS-X-PROFILE ****

STAGE	CO	PROPANE	PD	MEOH	MMA
1	0.0013484	0.00012453	0.0076203	0.52131	0.46732
2	0.000045882	0.000016270	0.0010780	0.36591	0.62682
3	0.21502E-06	0.29577E-05	0.00021417	0.36096	0.63273
9	0.0	0.14924E-10	0.25807E-08	0.012573	0.97799
10	0.0	0.96547E-12	0.21540E-09	0.0024063	0.98659
11	0.0	0.42859E-13	0.12414E-10	0.00032028	0.98449

**** MASS-X-PROFILE ****

STAGE	MC	ACID	P-MET-01
1	0.0022523	0.83039E-06	0.000019955
2	0.0060972	0.27199E-05	0.000023834
3	0.0060644	0.26859E-05	0.000023537
9	0.0094226	0.15058E-05	0.000013394
10	0.010990	0.14117E-05	0.000012836
11	0.015115	0.71747E-05	0.000062856

**** MASS-Y-PROFILE ****

STAGE	CO	PROPANE	PD	MEOH	MMA
1	0.65711	0.00082679	0.046724	0.19100	0.10429
2	0.020285	0.00014481	0.0087496	0.51178	0.45684
3	0.000073895	0.000026203	0.0017361	0.58912	0.40845
9	0.0	0.27398E-09	0.37201E-07	0.072631	0.92134
10	0.0	0.18873E-10	0.32624E-08	0.015825	0.97626
11	0.0	0.11910E-11	0.26503E-09	0.0029164	0.98710

**** MASS-Y-PROFILE ****

STAGE	MC	ACID	P-MET-01
1	0.000050895	0.32067E-12	0.37948E-09
2	0.0021887	0.80643E-06	0.33363E-05
3	0.00059152	0.35513E-10	0.10094E-07
9	0.0060295	0.58012E-09	0.14351E-06
10	0.0079117	0.11220E-08	0.26532E-06
11	0.0099819	0.26159E-08	0.60680E-06

****
***** HYDRAULIC PARAMETERS *****
****

*** DEFINITIONS ***

MARANGONI INDEX = SIGMA - SIGMATO
FLOW PARAM = (ML/MV)*SQRT(RHOV/RHOL)
QR = QV*SQRT(RHOV/(RHOL-RHOV))
F FACTOR = QV*SQRT(RHOV)
WHERE:
SIGMA IS THE SURFACE TENSION OF LIQUID FROM THE STAGE
SIGMATO IS THE SURFACE TENSION OF LIQUID TO THE STAGE
ML IS THE MASS FLOW OF LIQUID FROM THE STAGE
MV IS THE MASS FLOW OF VAPOR TO THE STAGE
RHOL IS THE MASS DENSITY OF LIQUID FROM THE STAGE
RHOV IS THE MASS DENSITY OF VAPOR TO THE STAGE
QV IS THE VOLUMETRIC FLOW RATE OF VAPOR TO THE STAGE

	MASS FLOW LB/HR		VOLUME FLOW CUFT/HR		MOLECULAR WEIGHT	
STAGE	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO
1	33934.	34943.	647.27	0.15382E+06	47.167	46.505
2	34841.	43203.	682.41	0.17315E+06	56.273	53.537
3	35282.	22074.	691.68	0.10039E+06	56.653	44.979
9	62970.	49762.	1232.8	0.11450E+06	97.513	96.861
10	67229.	54021.	1333.5	0.12132E+06	99.608	99.501
11	13208.	54021.	262.97	0.12132E+06	100.05	99.501

	DENSITY LB/CUFT		VISCOSITY CP		SURFACE TENSION DYNE/CM
STAGE	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO	LIQUID FROM
1	52.427	0.22716	0.40138	0.011398	21.056
2	51.056	0.24951	0.28545	0.011611	17.721
3	51.010	0.21989	0.28239	0.011319	17.596
9	51.078	0.43460	0.23108	0.010344	15.494
10	50.415	0.44526	0.21857	0.010310	14.604
11	50.226	0.44526	0.21530	0.010310	14.362

STAGE	MARANGONI INDEX DYNE/CM	FLOW PARAM	QR CUFT/HR	REDUCED F-FACTOR (LB-CUFT)**.5/HR
1		0.063925	10147.	73314.
2	-3.3353	0.056376	12134.	86492.
3	-0.12540	0.10494	6605.4	47075.
9	-1.6586	0.11673	10607.	75483.
10	-0.88958	0.11696	11453.	80957.
11	-0.24247	0.023021	11474.	80957.

```
**************************************
***** TRAY SIZING CALCULATIONS *****
**************************************

********************
*** SECTION   1 ***
********************

STARTING STAGE NUMBER                                    2
ENDING STAGE NUMBER                                     10
FLOODING CALCULATION METHOD                           FAIR

DESIGN PARAMETERS
-----------------
PEAK CAPACITY FACTOR                                   1.0
SYSTEM FOAMING FACTOR                                  1.0
FLOODING FACTOR                                       0.85
MINIMUM COLUMN DIAMETER              FT                1.0
MINIMUM DC AREA/COLUMN AREA                            0.1
HOLE AREA/ACTIVE AREA                                 0.12

TRAY SPECIFICATIONS
-------------------
TRAY TYPE                                             SIEVE
NUMBER OF PASSES                                          1
TRAY SPACING                         FT                1.67

      ***** SIZING RESULTS @ STAGE WITH MAXIMUM DIAMETER *****

STAGE WITH MAXIMUM DIAMETER                              10
COLUMN DIAMETER                      FT             4.99874
DC AREA/COLUMN AREA                                0.100000
DOWNCOMER VELOCITY                   FT/SEC         0.18875
WEIR LENGTH                          FT             3.63217

                **** SIZING PROFILES ****
```

STAGE	DIAMETER FT	TOTAL AREA SQFT	ACTIVE AREA SQFT	SIDE DC AREA SQFT
2	4.6846	17.236	13.788	1.7236
3	3.6818	10.646	8.5171	1.0646
7	4.0716	13.020	10.416	1.3020
8	4.3810	15.074	12.060	1.5074
9	4.7812	17.954	14.363	1.7954
10	4.9987	19.625	15.700	1.9625

BLOCK: D750 MODEL: RADFRAC

```
INLETS   - 690        STAGE  80
           815A       STAGE   1
  OUTLETS  - 799      STAGE   1
           755        STAGE   1
           775        STAGE  88
  PROPERTY OPTION SET:   UNIQUAC   UNIQUAC / IDEAL GAS

                    ***  MASS AND ENERGY BALANCE  ***
                                 IN                OUT          RELATIVE DIFF.
 TOTAL BALANCE
   MOLE(LBMOL/HR)              132.019           132.019          0.0
   MASS(LB/HR)                 13208.8           13208.8          0.289890E-09
   ENTHALPY(BTU/HR  )      -0.213723E+08     -0.217561E+08        0.0176437


                    ************************
                    ****  INPUT DATA  ****
                    ************************

****   INPUT PARAMETERS   ****

 NUMBER OF STAGES                                                    88
 ALGORITHM OPTION                                                    STANDARD
 ABSORBER OPTION                                                     NO
 INITIALIZATION OPTION                                               STANDARD
 HYDRAULIC PARAMETER CALCULATIONS                                    NO
 INSIDE LOOP CONVERGENCE METHOD                                      BROYDEN
 DESIGN SPECIFICATION METHOD                                         NESTED
 MAXIMUM NO. OF OUTSIDE LOOP ITERATIONS                               100
 MAXIMUM NO. OF INSIDE LOOP ITERATIONS                                 10
 MAXIMUM NUMBER OF FLASH ITERATIONS                                    50
 FLASH TOLERANCE                                                      0.00010000
 OUTSIDE LOOP CONVERGENCE TOLERANCE                                   0.00010000

****   COL-SPECS   ****

 MOLAR VAPOR DIST / TOTAL DIST                                        0.010000
 MOLAR REFLUX RATIO                                                   2.25959
 DISTILLATE TO FEED RATIO                                             0.96500

****    PROFILES   ****

 P-SPEC          STAGE   1  PRES, PSI                                14.6959

**** TRAY MURPHREE EFFICIENCY ****

                 STAGE   1  EFFICIENCY                                1.0000
                         2                                           0.70000
                        87                                           0.70000
                        88                                           1.0000
```

```
                    **********************
                    ****  RESULTS  ****
                    **********************

***   COMPONENT SPLIT FRACTIONS   ***

                              OUTLET STREAMS
                              --------------
                  799           755           775
 COMPONENT:
 PROPANE       0.28760       0.71240      0.55000E-16
 PD            0.23937       0.76063      0.13435E-14
 MEOH          0.091118      0.90888      0.92476E-09
 MMA           0.0097164     0.97016      0.020126
 MC            0.50539E-08   0.82478E-06  1.0000
 ACID          0.0           0.0          1.0000
 P-MET-01      0.32209E-05   0.083928     0.91607

***    SUMMARY OF KEY RESULTS    ***

 TOP STAGE TEMPERATURE              F                    212.
 BOTTOM STAGE TEMPERATURE           F                    253.
 TOP STAGE LIQUID FLOW              LBMOL/HR             601.
 BOTTOM STAGE LIQUID FLOW           LBMOL/HR               4.62
 TOP STAGE VAPOR FLOW               LBMOL/HR               1.27
 BOTTOM STAGE VAPOR FLOW            LBMOL/HR             712.
 MOLAR REFLUX RATIO                                        4.7
 MOLAR BOILUP RATIO                                     154.
 CONDENSER DUTY (W/O SUBCOOL)       BTU/HR          -10,600,000
 REBOILER DUTY                      BTU/HR           10,200,000


   ****   MANIPULATED VARIABLES   ****
                                                 BOUNDS
 CALCULATED
                                          LOWER          UPPER          VALUE
   MOLAR REFLUX RATIO                    0.0100         5.0000         4.7230

   ****    DESIGN SPECIFICATIONS   ****

  NO  SPEC-TYPE     QUALIFIERS                UNIT       SPECIFIED
 CALCULATED
                                                          VALUE          VALUE
   1  MOLE-FRAC     STREAMS: 755                          0.99904        0.99904
                    COMPS:   MMA

****   MAXIMUM FINAL RELATIVE ERRORS   ****

 DEW POINT                          0.14991E-04  STAGE= 72
 BUBBLE POINT                       0.16963E-04  STAGE= 75
 COMPONENT MASS BALANCE             0.24926E-05  STAGE= 80 COMP=MEOH
 ENERGY BALANCE                     0.41063E-05  STAGE= 88
```

**** PROFILES ****

NOTE REPORTED VALUES FOR STAGE LIQUID AND VAPOR RATES ARE THE FLOWS FROM THE STAGE EXCLUDING ANY SIDE PRODUCT. FOR THE FIRST STAGE, THE REPORTED VAPOR FLOW IS THE VAPOR DISTILLATE FLOW. FOR THE LAST STAGE, THE REPORTED LIQUID FLOW IS THE LIQUID BOTTOMS FLOW.

STAGE	TEMPERATURE F	PRESSURE PSI	ENTHALPY BTU/LBMOL LIQUID	ENTHALPY BTU/LBMOL VAPOR	HEAT DUTY BTU/HR
1	211.58	14.696	-0.16512E+06	-0.15003E+06	-.10596+08
2	212.42	14.796	-0.16513E+06	-0.15056E+06	
73	237.43	21.896	-0.16367E+06	-0.14965E+06	
74	237.82	21.996	-0.16363E+06	-0.14961E+06	
75	238.23	22.096	-0.16357E+06	-0.14957E+06	
78	239.57	22.396	-0.16337E+06	-0.14942E+06	
79	240.07	22.496	-0.16329E+06	-0.14936E+06	
80	240.55	22.596	-0.16321E+06	-0.14928E+06	
81	241.29	22.696	-0.16306E+06	-0.14915E+06	
87	249.48	23.296	-0.16093E+06	-0.14722E+06	
88	252.78	23.396	-0.16002E+06	-0.14660E+06	.10212+08

STAGE	FLOW RATE LBMOL/HR LIQUID	FLOW RATE LBMOL/HR VAPOR	FEED RATE LBMOL/HR LIQUID	FEED RATE LBMOL/HR VAPOR	FEED RATE LBMOL/HR MIXED	PRODUCT RATE LBMOL/HR LIQUID	PRODUCT RATE LBMOL/HR VAPOR
1	601.7	1.274	0.0062336			126.1247	1.2739
2	602.7	729.1					
73	614.5	741.9					
74	614.4	741.9					
75	614.4	741.8					
78	614.0	741.5					
79	613.9	741.3			15.6382		
80	729.8	725.6	116.3749				
81	729.2	725.2					
87	716.9	716.8					
88	4.621	712.3					4.6206

**** MASS FLOW PROFILES ****

STAGE	FLOW RATE LB/HR LIQUID	FLOW RATE LB/HR VAPOR	FEED RATE LB/HR LIQUID	FEED RATE LB/HR VAPOR	FEED RATE LB/HR MIXED	PRODUCT RATE LB/HR LIQUID	PRODUCT RATE LB/HR VAPOR
1	0.6020E+05	126.7	0.7738			0.12619+05	126.7292
2	0.6033E+05	0.7295E+05					
73	0.6152E+05	0.7426E+05					
74	0.6152E+05	0.7426E+05					
75	0.6151E+05	0.7426E+05					
78	0.6147E+05	0.7423E+05					
79	0.6146E+05	0.7421E+05			1560.6571		
80	0.7306E+05	0.7264E+05	0.11647+05				
81	0.7300E+05	0.7260E+05					
87	0.7178E+05	0.7176E+05					
88	462.9	0.7131E+05					462.8977

**** MOLE-X-PROFILE ****

STAGE	PROPANE	PD	MEOH	MMA	MC
1	0.72510E-13	0.24681E-10	0.00095139	0.99904	0.13039E-07
2	0.25494E-14	0.10991E-11	0.00012575	0.99987	0.18253E-07
73	0.0	0.21680E-12	0.000020948	0.98005	0.019924
74	0.0	0.21707E-12	0.000021126	0.97623	0.023740
75	0.0	0.21731E-12	0.000021335	0.97172	0.028248
78	0.0	0.21783E-12	0.000022202	0.95289	0.047084
79	0.0	0.21858E-12	0.000022595	0.94439	0.055576
80	0.0	0.77775E-13	0.000015831	0.93706	0.062910
81	0.0	0.41989E-14	0.26036E-05	0.91926	0.080717
87	0.0	0.0	0.14163E-09	0.67001	0.32995
88	0.0	0.0	0.26423E-10	0.56570	0.43153

**** MOLE-X-PROFILE ****

STAGE	ACID	P-MET-01
1	0.0	0.85982E-05
2	0.0	0.85845E-05
73	0.24955E-12	0.84418E-05
74	0.83316E-12	0.84428E-05
75	0.27816E-11	0.84446E-05
78	0.10352E-09	0.84731E-05
79	0.34561E-09	0.85236E-05
80	0.13242E-05	0.000016332
81	0.13254E-05	0.000016360
87	0.14091E-05	0.000038722
88	0.00020910	0.0025617

**** MOLE-Y-PROFILE ****

STAGE	PROPANE	PD	MEOH	MMA	MC
1	0.28980E-11	0.76894E-09	0.0094426	0.99056	0.79101E-08
2	0.77448E-13	0.25982E-10	0.00096623	0.99903	0.13030E-07
73	0.17737E-13	0.56960E-11	0.00019519	0.98597	0.013833
74	0.17737E-13	0.56962E-11	0.00019531	0.98330	0.016503
75	0.17738E-13	0.56966E-11	0.00019547	0.98014	0.019663
78	0.17746E-13	0.56994E-11	0.00019615	0.96685	0.032956
79	0.17751E-13	0.57009E-11	0.00019647	0.96081	0.038993
80	0.36703E-14	0.14470E-11	0.000099815	0.95310	0.046801
81	0.0	0.78271E-13	0.000015931	0.93942	0.060562
87	0.0	0.0	0.63111E-09	0.73315	0.26684
88	0.0	0.0	0.14238E-09	0.67069	0.32929

**** MOLE-Y-PROFILE ****

STAGE	ACID	P-MET-01
1	0.0	0.32667E-07
2	0.0	0.33555E-07
73	0.61910E-13	0.50944E-07
74	0.20670E-12	0.51373E-07
75	0.69008E-12	0.51908E-07
78	0.25680E-10	0.58655E-07
79	0.85733E-10	0.71477E-07
80	0.26007E-09	0.10708E-06
81	0.27650E-09	0.11293E-06
87	0.18620E-07	0.68950E-05
88	0.61800E-07	0.000022356

**** K-VALUES ****

STAGE	PROPANE	PD	MEOH	MMA	MC
1	39.967	31.155	9.9251	0.99151	0.60663
2	40.062	31.212	10.002	0.99888	0.61303
73	33.948	26.273	9.3221	1.0072	0.63760
74	33.909	26.240	9.2490	1.0086	0.63880
75	33.876	26.213	9.1647	1.0103	0.64019
78	33.816	26.161	8.8337	1.0173	0.64570
79	33.813	26.157	8.6939	1.0205	0.64812
80	33.803	26.147	8.5774	1.0234	0.65032
81	33.872	26.198	8.3113	1.0303	0.65527
87	35.419	27.386	5.9347	1.1342	0.72763
88	36.273	28.046	5.3887	1.1856	0.76307

**** K-VALUES ****

STAGE	ACID	P-MET-01
1	0.000089878	0.0037993
2	0.000092669	0.0038949
73	0.00017441	0.0060122
74	0.00017632	0.0060571
75	0.00017835	0.0061051
78	0.00018551	0.0062734
79	0.00018836	0.0063400
80	0.00019106	0.0064030
81	0.00019579	0.0065143
87	0.00026173	0.0080062
88	0.00029554	0.0087268

**** MASS-X-PROFILE ****

STAGE	PROPANE	PD	MEOH	MMA	MC
1	0.31957E-13	0.98834E-11	0.00030468	0.99968	0.13048E-07
2	0.11230E-14	0.43986E-12	0.000040248	0.99995	0.18255E-07
73	0.0	0.86760E-13	0.67043E-05	0.98006	0.019925
74	0.0	0.86868E-13	0.67613E-05	0.97624	0.023741
75	0.0	0.86965E-13	0.68283E-05	0.97173	0.028249
78	0.0	0.87173E-13	0.71056E-05	0.95290	0.047086
79	0.0	0.87471E-13	0.72316E-05	0.94440	0.055578
80	0.0	0.31124E-13	0.50665E-05	0.93706	0.062912
81	0.0	0.16803E-14	0.83326E-06	0.91926	0.080719
87	0.0	0.0	0.45329E-10	0.67000	0.32995
88	0.0	0.0	0.84512E-11	0.56535	0.43128

**** MASS-X-PROFILE ****

STAGE	ACID	P-MET-01
1	0.0	0.000010668
2	0.0	0.000010645
73	0.24447E-12	0.000010467
74	0.81621E-12	0.000010469
75	0.27250E-11	0.000010471
78	0.10142E-09	0.000010506
79	0.33858E-09	0.000010569
80	0.12973E-05	0.000020250
81	0.12984E-05	0.000020285
87	0.13804E-05	0.000048013
88	0.00020472	0.0031744

**** MASS-Y-PROFILE ****

STAGE	PROPANE	PD	MEOH	MMA	MC
1	0.12847E-11	0.30970E-09	0.0030416	0.99696	0.79614E-08
2	0.34134E-13	0.10404E-10	0.00030944	0.99969	0.13039E-07
73	0.78131E-14	0.22797E-11	0.000062478	0.98610	0.013835
74	0.78133E-14	0.22798E-11	0.000062518	0.98343	0.016505
75	0.78138E-14	0.22800E-11	0.000062567	0.98027	0.019667
78	0.78173E-14	0.22811E-11	0.000062786	0.96698	0.032961
79	0.78194E-14	0.22817E-11	0.000062889	0.96094	0.038999
80	0.16167E-14	0.57910E-12	0.000031947	0.95316	0.046805
81	0.0	0.31323E-13	0.50988E-05	0.93943	0.060564
87	0.0	0.0	0.20198E-09	0.73315	0.26684
88	0.0	0.0	0.45568E-10	0.67068	0.32929

**** MASS-Y-PROFILE ****

STAGE	ACID	P-MET-01
1	0.0	0.40767E-07
2	0.0	0.41633E-07
73	0.60658E-13	0.63175E-07
74	0.20252E-12	0.63708E-07
75	0.67613E-12	0.64371E-07
78	0.25160E-10	0.72738E-07
79	0.83999E-10	0.88639E-07
80	0.25479E-09	0.13278E-06
81	0.27088E-09	0.14003E-06
87	0.18241E-07	0.85493E-05
88	0.60542E-07	0.000027720

****
***** HYDRAULIC PARAMETERS *****
****

*** DEFINITIONS ***

MARANGONI INDEX = SIGMA - SIGMATO
FLOW PARAM = (ML/MV)*SQRT(RHOV/RHOL)
QR = QV*SQRT(RHOV/(RHOL-RHOV))
F FACTOR = QV*SQRT(RHOV)

WHERE:
SIGMA IS THE SURFACE TENSION OF LIQUID FROM THE STAGE
SIGMATO IS THE SURFACE TENSION OF LIQUID TO THE STAGE
ML IS THE MASS FLOW OF LIQUID FROM THE STAGE
MV IS THE MASS FLOW OF VAPOR TO THE STAGE
RHOL IS THE MASS DENSITY OF LIQUID FROM THE STAGE
RHOV IS THE MASS DENSITY OF VAPOR TO THE STAGE
QV IS THE VOLUMETRIC FLOW RATE OF VAPOR TO THE STAGE

	MASS FLOW LB/HR		VOLUME FLOW CUFT/HR		MOLECULAR WEIGHT	
STAGE	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO
1	72821.	72947.	1377.5	0.35541E+06	100.05	100.05
2	60334.	73079.	1142.1	0.35373E+06	100.11	100.10
75	61510.	74255.	1191.1	0.25044E+06	100.12	100.10
78	61467.	74212.	1192.1	0.24746E+06	100.12	100.10
79	61458.	74203.	1192.7	0.24759E+06	100.12	100.10
80	73065.	72602.	1418.8	0.24035E+06	100.12	100.12
81	73003.	72540.	1419.1	0.23938E+06	100.12	100.12
87	71777.	71315.	1413.2	0.23277E+06	100.12	100.12
88	462.90	71315.	9.1513	0.23277E+06	100.18	100.12

	DENSITY LB/CUFT		VISCOSITY CP		SURFACE TENSION DYNE/CM
STAGE	LIQUID FROM	VAPOR TO	LIQUID FROM	VAPOR TO	LIQUID FROM
1	52.864	0.20525	0.27273	0.0094359	18.188
2	52.827	0.20659	0.27175	0.0094413	18.132
73	51.688	0.29417	0.24424	0.0098114	16.454
74	51.666	0.29534	0.24381	0.0098157	16.431
75	51.643	0.29649	0.24336	0.0098199	16.408
78	51.560	0.29989	0.24183	0.0098322	16.333
79	51.527	0.29970	0.24126	0.0098348	16.307
80	51.497	0.30207	0.24072	0.0098373	16.282
81	51.443	0.30303	0.23983	0.0098395	16.247
87	50.791	0.30637	0.22997	0.0098407	15.923
88	50.583	0.30637	0.22746	0.0098407	15.860

STAGE	MARANGONI INDEX DYNE/CM	FLOW PARAM	QR CUFT/HR	REDUCED F-FACTOR (LB-CUFT)**.5/HR
1		0.062203	22189.	0.16101E+06
2	-0.055810	0.051630	22165.	0.16078E+06
73	-0.022619	0.062493	19099.	0.13692E+06
74	-0.023023	0.062630	19065.	0.13665E+06
75	-0.023507	0.062766	19031.	0.13637E+06
78	-0.025547	0.063167	18928.	0.13552E+06
79	-0.026455	0.063165	18938.	0.13554E+06
80	-0.030329	0.077076	18462.	0.13210E+06
81	-0.034319	0.077240	18427.	0.13178E+06
87	-0.072317	0.078169	18133.	0.12884E+06
88	-0.062911	0.00050516	18171.	0.12884E+06

```
**************************************
***** TRAY SIZING CALCULATIONS *****
**************************************

********************
*** SECTION   1 ***
********************
STARTING STAGE NUMBER                                          2
ENDING STAGE NUMBER                                           87
FLOODING CALCULATION METHOD                                 FAIR

DESIGN PARAMETERS
-----------------
PEAK CAPACITY FACTOR                                        1.0
SYSTEM FOAMING FACTOR                                       1.0
FLOODING FACTOR                                             0.85
MINIMUM COLUMN DIAMETER                  FT                 1.0
MINIMUM DC AREA/COLUMN AREA                                 0.1
HOLE AREA/ACTIVE AREA                                       0.12

TRAY SPECIFICATIONS
-------------------
TRAY TYPE                                                 SIEVE
NUMBER OF PASSES                                              1
TRAY SPACING                             FT                1.67
```

***** SIZING RESULTS @ STAGE WITH MAXIMUM DIAMETER *****

STAGE WITH MAXIMUM DIAMETER		2
COLUMN DIAMETER	FT	6.26572
DC AREA/COLUMN AREA		0.100000
DOWNCOMER VELOCITY	FT/SEC	0.10289
WEIR LENGTH	FT	4.55278

**** SIZING PROFILES ****

STAGE	DIAMETER FT	TOTAL AREA SQFT	ACTIVE AREA SQFT	SIDE DC AREA SQFT
2	6.2657	30.834	24.667	3.0834
3	6.2611	30.789	24.631	3.0789
79	5.9648	27.943	22.355	2.7943
80	6.0063	28.333	22.667	2.8333
81	6.0031	28.304	22.643	2.8304
86	5.9843	28.127	22.501	2.8127
87	5.9743	28.032	22.426	2.8032

BLOCK: H410 MODEL: HEATX

```
HOT SIDE:
---------
INLET STREAM:          290
OUTLET STREAM:         410
PROPERTY OPTION SET:   UNIQUAC   UNIQUAC / IDEAL GAS
COLD SIDE:
----------
INLET STREAM:          922
OUTLET STREAM:         982
PROPERTY OPTION SET:   UNIQUAC   UNIQUAC / IDEAL GAS
```

*** MASS AND ENERGY BALANCE ***

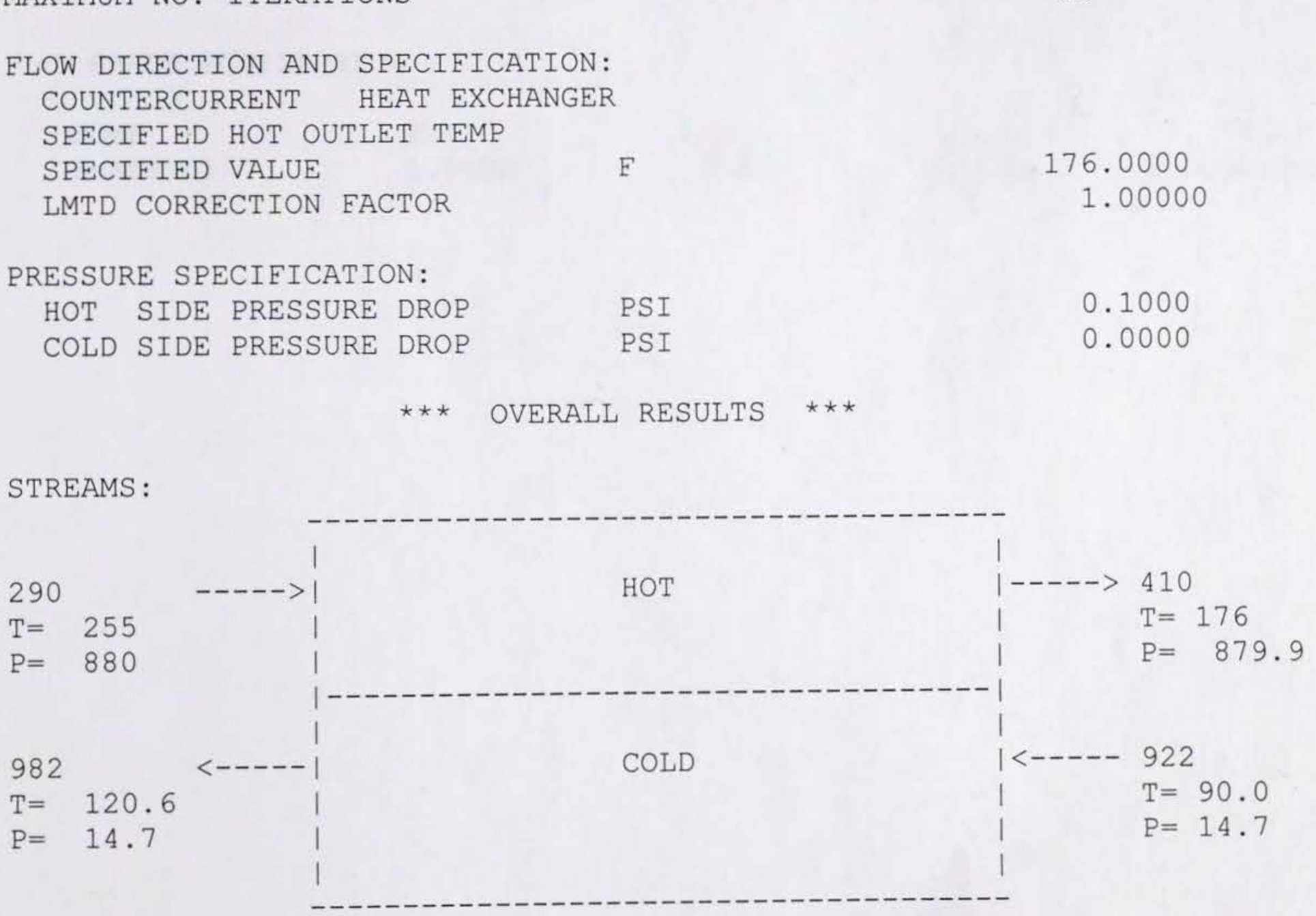
	IN	OUT	RELATIVE DIFF.
TOTAL BALANCE			
MOLE(LBMOL/HR)	3193.12	3193.12	0.0
MASS(LB/HR)	66972.2	66972.2	0.0
ENTHALPY(BTU/HR)	-0.358920E+09	-0.358920E+09	0.166067E-15

*** INPUT DATA ***

```
FLASH SPECS FOR HOT SIDE:
TWO    PHASE      FLASH
MAXIMUM NO. ITERATIONS                                  30

FLASH SPECS FOR COLD SIDE:
TWO    PHASE      FLASH
MAXIMUM NO. ITERATIONS                                  30

FLOW DIRECTION AND SPECIFICATION:
  COUNTERCURRENT   HEAT EXCHANGER
  SPECIFIED HOT OUTLET TEMP
  SPECIFIED VALUE                F                     176.0000
  LMTD CORRECTION FACTOR                                 1.00000

PRESSURE SPECIFICATION:
  HOT  SIDE PRESSURE DROP        PSI                     0.1000
  COLD SIDE PRESSURE DROP        PSI                     0.0000
```

*** OVERALL RESULTS ***

STREAMS:



DUTY AND AREA:		
CALCULATED HEAT DUTY	BTU/HR	1,440,000.
CALCULATED (REQUIRED) AREA	SQFT	88.9
HEAT TRANSFER COEFFICIENT:		
AVERAGE COEFFICIENT (DIRTY)	BTU/HR-SQFT-R	150
LOG-MEAN TEMPERATURE DIFFERENCE:		
LMTD CORRECTION FACTOR		1.0000
LMTD (CORRECTED)	F	108.5
PRESSURE DROP:		
SHELLSIDE, TOTAL	PSI	0.1000
TUBESIDE, TOTAL	PSI	0.0000

BLOCK: M810 MODEL: HEATER

```
INLET STREAM:              805
OUTLET STREAM:             810
PROPERTY OPTION SET:       UNIQUAC   UNIQUAC / IDEAL GAS

                    ***  MASS AND ENERGY BALANCE  ***
                                  IN                  OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)          0.0129166           0.0129166            0.0
    MASS(LB/HR    )          1.60346             1.60346             0.0
    ENTHALPY(BTU/HR  )      -1773.37            -1726.19           -0.0266083

                      ***  INPUT DATA  ***
TWO    PHASE  TP  FLASH
SPECIFIED TEMPERATURE                  F                          150.800
SPECIFIED PRESSURE                     PSI                         14.6959
MAXIMUM NO. ITERATIONS                                             30
CONVERGENCE TOLERANCE                                               0.00010000

                      ***  RESULTS  ***
OUTLET TEMPERATURE     F                                          150.80
OUTLET PRESSURE        PSI                                        14.696
HEAT DUTY              BTU/HR                                     47.186
OUTLET VAPOR FRACTION                                            0.0

V-L PHASE EQUILIBRIUM :

   COMP                F(I)          X(I)          Y(I)          K(I)
   P-MET-01            1.0000        1.0000        1.0000        0.00027431
```

BLOCK: P110 MODEL: PUMP

```
INLET STREAM:                  110
OUTLET STREAM:                 150
PROPERTY OPTION SET:    UNIQUAC   UNIQUAC / IDEAL GAS

                    ***  MASS AND ENERGY BALANCE  ***
                                 IN                OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)             295.500           295.500          0.0
    MASS(LB/HR    )            12431.8           12431.8          0.0
    ENTHALPY(BTU/HR  )      0.328378E+07      0.330815E+07       -0.007

                         ***  INPUT DATA  ***
OUTLET PRESSURE (PSI)                                            326.600
DRIVER EFFICIENCY                                                  1.0

FLASH SPECIFICATIONS:
LIQUID PHASE CALCULATION
NO FLASH PERFORMED
MAXIMUM NUMBER OF ITERATIONS                                        30
TOLERANCE                                                       0.00010000

                         ***  RESULTS  ***
VOLUMETRIC FLOW RATE (CUFT/HR )                                  372.
PRESSURE CHANGE (PSI     )                                       151.
NPSH AVAILABLE  (FT      )                                       242.
FLUID POWER (HP      )                                            4.1
BRAKE POWER (HP      )                                            9.6
ELECTRICITY (KW      )                                            7.1
PUMP EFFICIENCY USED                                              0.4
NET WORK (HP      )                                              -9.6
```

BLOCK: P210 MODEL: PUMP

```
INLET STREAM:                210
OUTLET STREAM:               220
PROPERTY OPTION SET:         UNIQUAC   UNIQUAC / IDEAL GAS

                      ***  MASS AND ENERGY BALANCE  ***
                                    IN                OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)              140.356           140.356          0.0
    MASS(LB/HR    )             4497.29           4497.29          0.0
    ENTHALPY(BTU/HR  )      -0.143966E+08     -0.143960E+08    -0.0000404361

                         ***  INPUT DATA  ***
OUTLET PRESSURE (PSI     )                                      25.0000
DRIVER EFFICIENCY                                                1.00000

FLASH SPECIFICATIONS:
LIQUID PHASE CALCULATION
NO FLASH PERFORMED
MAXIMUM NUMBER OF ITERATIONS                                     30
TOLERANCE                                                        0.00010000

                         ***  RESULTS  ***
VOLUMETRIC FLOW RATE (CUFT/HR )                                  90.2
PRESSURE CHANGE (PSI     )                                       10.3
NPSH AVAILABLE  (FT      )                                       35.4
FLUID POWER (HP      )                                           0.067
BRAKE POWER (HP      )                                           0.22
ELECTRICITY (KW      )                                           0.17
PUMP EFFICIENCY USED                                             0.296
NET WORK (HP     )                                              -0.229
```

BLOCK: P230 MODEL: PUMP

```
INLET STREAM:                230
OUTLET STREAM:               250
PROPERTY OPTION SET:         UNIQUAC   UNIQUAC / IDEAL GAS

                      ***  MASS AND ENERGY BALANCE  ***
                                 IN                OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)             296.266           296.266          0.0
    MASS(LB/HR    )            11851.2           11851.2          0.0
    ENTHALPY(BTU/HR  )      -0.322702E+08     -0.322429E+08    -0.000847023

                         ***  INPUT DATA  ***
OUTLET PRESSURE (PSI     )                                      257.100
DRIVER EFFICIENCY                                                 1.00000

FLASH SPECIFICATIONS:
LIQUID PHASE CALCULATION
NO FLASH PERFORMED
MAXIMUM NUMBER OF ITERATIONS                                        30
TOLERANCE                                                         0.00010000

                          ***  RESULTS  ***
VOLUMETRIC FLOW RATE (CUFT/HR )                                   230.2
PRESSURE CHANGE (PSI     )                                        227.7
NPSH AVAILABLE  (FT      )                                         27.8
FLUID POWER (HP      )                                            3.8
BRAKE POWER (HP      )                                           10.7
ELECTRICITY (KW      )                                            8.01
PUMP EFFICIENCY USED                                              0.35
NET WORK (HP     )                                              -10.74
```

BLOCK: P270 MODEL: PUMP

```
INLET STREAM:                275
OUTLET STREAM:               290
PROPERTY OPTION SET:         UNIQUAC   UNIQUAC / IDEAL GAS

                      ***  MASS AND ENERGY BALANCE  ***
                                    IN                  OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)                428.799             428.799          0.0
    MASS(LB/HR    )               17172.2             17172.2          0.0
    ENTHALPY(BTU/HR  )         -0.201118E+08       -0.200014E+08    -0.00549009

                         ***  INPUT DATA  ***
OUTLET PRESSURE (PSI     )                                          880.000
DRIVER EFFICIENCY                                                     1.00000

FLASH SPECIFICATIONS:
LIQUID PHASE CALCULATION
NO FLASH PERFORMED
MAXIMUM NUMBER OF ITERATIONS                                            30
TOLERANCE                                                           0.00010000

                         ***  RESULTS  ***
VOLUMETRIC FLOW RATE (CUFT/HR )                                      446.97
PRESSURE CHANGE (PSI     )                                           608.1
NPSH AVAILABLE  (FT      )                                           -0.225
FLUID POWER (HP      )                                               19.77
BRAKE POWER (HP      )                                               43.4
ELECTRICITY (KW      )                                               32.4
PUMP EFFICIENCY USED                                                  0.456
NET WORK (HP     )                                                  -43.40
```

BLOCK: P390 MODEL: PUMP

```
INLET STREAM:                MIXEDCAT
OUTLET STREAM:               395

PROPERTY OPTION SET:   UNIQUAC   UNIQUAC / IDEAL GAS

                    ***  MASS AND ENERGY BALANCE  ***
                                 IN                OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)                7.63796           7.63796          0.0
    MASS(LB/HR    )               719.386           719.386          0.0
    ENTHALPY(BTU/HR  )       -0.134500E+07     -0.133811E+07    -0.00511961

                         ***  INPUT DATA  ***
 EQUIPMENT TYPE: PUMP
 OUTLET PRESSURE (PSI     )                                      880.000
 DRIVER EFFICIENCY                                                 1.00000

 FLASH SPECIFICATIONS:
 LIQUID PHASE CALCULATION
 NO FLASH PERFORMED
 MAXIMUM NUMBER OF ITERATIONS                                        30
 TOLERANCE                                                         0.00010000

                         ***  RESULTS  ***
 VOLUMETRIC FLOW RATE (CUFT/HR )                                   12.71
 PRESSURE CHANGE (PSI     )                                       865.3
 NPSH AVAILABLE  (FT      )                                       -13.04
 FLUID POWER (HP      )                                            0.80
 BRAKE POWER (HP      )                                            2.706
 ELECTRICITY (KW      )                                            2.01
 PUMP EFFICIENCY USED                                              0.296
 NET WORK (HP      )                                              -2.706
```

BLOCK: P670 MODEL: PUMP

```
INLET STREAM:                675
OUTLET STREAM:               690

PROPERTY OPTION SET:    UNIQUAC   UNIQUAC / IDEAL GAS

                      ***  MASS AND ENERGY BALANCE  ***
                                 IN                OUT          RELATIVE DIFF.
 TOTAL BALANCE
   MOLE(LBMOL/HR)              132.013           132.013          0.0
   MASS(LB/HR    )           13208.0           13208.0          -0.137719E-15
   ENTHALPY(BTU/HR  )     -0.213712E+08     -0.213714E+08       0.855951E-05

                        ***  INPUT DATA  ***
OUTLET PRESSURE (PSI     )                                    25.0000
DRIVER EFFICIENCY                                              1.00000

FLASH SPECIFICATIONS:
LIQUID PHASE CALCULATION
NO FLASH PERFORMED
MAXIMUM NUMBER OF ITERATIONS                                   30
TOLERANCE                                                      0.00010000

                        ***  RESULTS  ***
VOLUMETRIC FLOW RATE (CUFT/HR )                               263
PRESSURE CHANGE (PSI     )                                   -10.0
NPSH AVAILABLE  (FT      )                                    0.0
FLUID POWER (HP      )                                       -0.191
BRAKE POWER (HP      )                                       -0.0719
ELECTRICITY (KW      )                                       -0.0536
PUMP EFFICIENCY USED                                          0.376
NET WORK (HP      )                                           0.0719
```

BLOCK: P680 MODEL: PUMP

```
INLET STREAM:                  655
OUTLET STREAM:                 680
PROPERTY OPTION SET:    UNIQUAC   UNIQUAC / IDEAL GAS

                      ***  MASS AND ENERGY BALANCE  ***
                                   IN                OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)                155.910           155.910          0.0
    MASS(LB/HR    )              7353.86           7353.86          -0.123676E-15
    ENTHALPY(BTU/HR  )       -0.178741E+08     -0.178742E+08        0.386417E-05

                          ***  INPUT DATA  ***
OUTLET PRESSURE (PSI      )                                        25.0000
DRIVER EFFICIENCY                                                   1.00000

FLASH SPECIFICATIONS:
LIQUID PHASE CALCULATION
NO FLASH PERFORMED
MAXIMUM NUMBER OF ITERATIONS                                        30
TOLERANCE                                                           0.00010000

                           ***  RESULTS  ***
VOLUMETRIC FLOW RATE (CUFT/HR )                                   140.269
PRESSURE CHANGE (PSI      )                                        -9.00
NPSH AVAILABLE  (FT       )                                         0.0287
FLUID POWER (HP       )                                           -0.0918
BRAKE POWER (HP       )                                           -0.0271
ELECTRICITY (KW       )                                           -0.0202
PUMP EFFICIENCY USED                                               0.296
NET WORK (HP      )                                                0.0271
```

BLOCK: P770 MODEL: PUMP

```
INLET STREAM:          775
   OUTLET STREAM:          798
   PROPERTY OPTION SET:  UNIQUAC   UNIQUAC / IDEAL GAS

                      ***  MASS AND ENERGY BALANCE  ***

                                        IN              OUT    RELATIVE DIFF.
    TOTAL BALANCE
      MOLE(LBMOL/HR)                4.62068         4.62068         0.0
      MASS(LB/HR    )                462.898         462.898      -0.491196E-15
      ENTHALPY(BTU/HR  )           -739379.        -739370.       -0.124260E-04

                          ***  INPUT DATA  ***
OUTLET PRESSURE (PSI      )                                    25.0000
DRIVER EFFICIENCY                                               1.00000

FLASH SPECIFICATIONS:
LIQUID PHASE CALCULATION
NO FLASH PERFORMED
MAXIMUM NUMBER OF ITERATIONS                                    30
TOLERANCE                                                       0.00010000

                          ***  RESULTS  ***
VOLUMETRIC FLOW RATE (CUFT/HR )                                 9.15
PRESSURE CHANGE (PSI      )                                     1.604
NPSH AVAILABLE  (FT       )                                     0.0
FLUID POWER (HP       )                                         0.00107
BRAKE POWER (HP       )                                         0.00361
ELECTRICITY (KW       )                                         0.00269
PUMP EFFICIENCY USED                                            0.296
NET WORK (HP       )                                           -0.00361
```

BLOCK: P780 MODEL: PUMP

```
INLET STREAM:                 755
OUTLET STREAM:                780
PROPERTY OPTION SET:    UNIQUAC   UNIQUAC / IDEAL GAS

                      ***  MASS AND ENERGY BALANCE  ***
                                    IN                OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)                126.125           126.125          0.0
    MASS(LB/HR    )                12619.1           12619.1          0.0
    ENTHALPY(BTU/HR  )         -0.208256E+08     -0.208243E+08    -0.0000606004

                         ***  INPUT DATA  ***
OUTLET PRESSURE (PSI     )                                          25.0000
DRIVER EFFICIENCY                                                    1.00000

FLASH SPECIFICATIONS:
LIQUID PHASE CALCULATION
NO FLASH PERFORMED
MAXIMUM NUMBER OF ITERATIONS                                         30
TOLERANCE                                                            0.00010000

                           ***  RESULTS  ***
VOLUMETRIC FLOW RATE (CUFT/HR )                                     238.709
PRESSURE CHANGE (PSI     )                                           10.3041
NPSH AVAILABLE  (FT      )                                           0.0
FLUID POWER (HP      )                                               0.17888
BRAKE POWER (HP      )                                               0.49600
ELECTRICITY (KW      )                                               0.36987
PUMP EFFICIENCY USED                                                 0.36065
NET WORK (HP      )                                                 -0.49600
```

BLOCK: P815A MODEL: PUMP

```
INLET STREAM:              810A
OUTLET STREAM:             815A
PROPERTY OPTION SET:       UNIQUAC   UNIQUAC / IDEAL GAS


                      ***  MASS AND ENERGY BALANCE  ***
                                   IN                  OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)            0.623356E-02        0.623356E-02      0.0
    MASS(LB/HR    )           0.773829            0.773829          0.0
    ENTHALPY(BTU/HR  )         -833.058            -832.986         -0.0000864625

                         ***  INPUT DATA  ***
OUTLET PRESSURE (PSI     )                                          25.0000
DRIVER EFFICIENCY                                                    1.00000

FLASH SPECIFICATIONS:
LIQUID PHASE CALCULATION
NO FLASH PERFORMED
MAXIMUM NUMBER OF ITERATIONS                                         30
TOLERANCE                                                            0.00010000

                          ***  RESULTS  ***
VOLUMETRIC FLOW RATE (CUFT/HR )                                      0.011169
PRESSURE CHANGE (PSI     )                                          10.3041
NPSH AVAILABLE  (FT      )                                          30.5241
FLUID POWER (HP      )                                               0.836953-05
BRAKE POWER (HP      )                                               0.283082-04
ELECTRICITY (KW      )                                               0.211094-04
PUMP EFFICIENCY USED                                                 0.29566
NET WORK (HP      )                                                 -0.283082-04
```

BLOCK: P815B MODEL: PUMP

```
INLET STREAM:                 810B
OUTLET STREAM:                815B
PROPERTY OPTION SET:    UNIQUAC   UNIQUAC / IDEAL GAS

                      ***  MASS AND ENERGY BALANCE  ***
                                    IN                  OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)              0.451565E-02      0.451565E-02      0.0
    MASS(LB/HR    )             0.560569          0.560569          0.0
    ENTHALPY(BTU/HR   )         -603.475          -603.377          -0.000161983

                          ***  INPUT DATA  ***
 OUTLET PRESSURE (PSI     )                                        34.0000
 DRIVER EFFICIENCY                                                  1.00000

 FLASH SPECIFICATIONS:
 LIQUID PHASE CALCULATION
 NO FLASH PERFORMED
 MAXIMUM NUMBER OF ITERATIONS                                       30
 TOLERANCE                                                          0.00010000

                          ***  RESULTS  ***
 VOLUMETRIC FLOW RATE (CUFT/HR )                                    0.0080906
 PRESSURE CHANGE (PSI     )                                        19.3041
 NPSH AVAILABLE  (FT      )                                        30.5241
 FLUID POWER (HP      )                                             0.113586-04
 BRAKE POWER (HP      )                                             0.384182-04
 ELECTRICITY (KW      )                                             0.286484-04
 PUMP EFFICIENCY USED                                               0.29566
 NET WORK (HP      )                                              -0.384182-04
```

BLOCK: P815C MODEL: PUMP

```
INLET STREAM:                 810C
OUTLET STREAM:                815C
PROPERTY OPTION SET:          UNIQUAC   UNIQUAC / IDEAL GAS

                        ***  MASS AND ENERGY BALANCE  ***
                                      IN                  OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)              0.216741E-02        0.216741E-02          0.0
    MASS(LB/HR    )             0.269060            0.269060              0.0
    ENTHALPY(BTU/HR  )          -289.654            -287.551          -0.00726087

                            ***  INPUT DATA  ***
OUTLET PRESSURE (PSI     )                                          880.000
DRIVER EFFICIENCY                                                    1.00000

FLASH SPECIFICATIONS:
LIQUID PHASE CALCULATION
NO FLASH PERFORMED
MAXIMUM NUMBER OF ITERATIONS                                            30
TOLERANCE                                                           0.00010000

                            ***  RESULTS  ***
VOLUMETRIC FLOW RATE (CUFT/HR )                                     0.0038833
PRESSURE CHANGE (PSI     )                                        865.304
NPSH AVAILABLE  (FT      )                                         30.5241
FLUID POWER (HP      )                                             0.00024438
BRAKE POWER (HP      )                                             0.00082657
ELECTRICITY (KW      )                                             0.00061637
PUMP EFFICIENCY USED                                               0.29566
NET WORK (HP      )                                               -0.00082657
```

BLOCK: R150 MODEL: RYIELD

```
INLET STREAM:                150
OUTLET STREAM:               190
PROPERTY OPTION SET:    UNIQUAC   UNIQUAC / IDEAL GAS

                      ***  MASS AND ENERGY BALANCE  ***
                          IN            OUT        GENERATION   RELATIVE DIFF.
TOTAL BALANCE
MOLE(LBMOL/HR)          295.500       295.500  0.688394E-14  0.232959E-16
MASS(LB/HR    )         12431.8       12431.8       0.0
ENTHALPY(BTU/HR)    0.330815E+07  0.317422E+07 0.0404852

                          ***  INPUT DATA  ***
TWO    PHASE  TP  FLASH
SPECIFIED TEMPERATURE F                                        87.0000
PRESSURE DROP          PSI                                     60.0000
MAXIMUM NO. ITERATIONS                                         30
CONVERGENCE TOLERANCE                                           0.00010000

 MASS-YIELD
  SUBSTREAM MIXED   :
  PD         0.100         MA         0.900

INERTS: CO PROPYLEN PROPANE MEOH MMA MC ACID

                          ***  RESULTS  ***
OUTLET TEMPERATURE     F                                       87.000
OUTLET PRESSURE        PSI                                     266.60
HEAT DUTY              BTU/HR                                 -0.13393E+06
VAPOR FRACTION                                                 0.0

V-L PHASE EQUILIBRIUM :

   COMP                F(I)          X(I)          Y(I)          K(I)
   PROPYLEN         0.0050697     0.0050697     0.0074872     0.72352
   PROPANE          0.49493       0.49493       0.60094       0.59484
   PD               0.050000      0.050000      0.050656      0.49633
   MA               0.45000       0.45000       0.34092       0.37116
```

BLOCK: R450 MODEL: RSTOIC

```
INLET STREAMS:          395          340          410          815C
OUTLET STREAM:          450
PROPERTY OPTION SET:    UNIQUAC    UNIQUAC / IDEAL GAS

                  ***  MASS AND ENERGY BALANCE  ***
                        IN            OUT        GENERATION   RELATIVE DIFF.
TOTAL BALANCE
MOLE(LBMOL/HR)          593.439       327.490    -265.949        0.102462E-05
MASS(LB/HR    )         22289.5       22289.6                   -0.430992E-05
ENTHALPY(BTU/HR  )   -0.302433E+08 -0.424648E+08                  0.287803

                              ***  INPUT DATA  ***

SIMULTANEOUS REACTIONS
STOICHIOMETRY MATRIX:

 REACTION #   1:
  SUBSTREAM MIXED   :
  CO        -1.00    MA        -1.00    MEOH      -1.00    MMA         1.00

 REACTION #   2:
  SUBSTREAM MIXED   :
  CO        -1.00    MA        -1.00    MEOH      -1.00    MC          1.00


REACTION CONVERSION SPECS: NUMBER=    2
  REACTION #   1:
  SUBSTREAM:MIXED    KEY COMP:MA       CONV FRAC: 0.9850
  REACTION #   2:
  SUBSTREAM:MIXED    KEY COMP:MA       CONV FRAC: 0.01500

TWO    PHASE  TP  FLASH
SPECIFIED TEMPERATURE F                                  194.000
SPECIFIED PRESSURE    PSI                                870.226
MAXIMUM NO. ITERATIONS                                    30
CONVERGENCE TOLERANCE                                      0.00010000

                        ***  RESULTS  ***
OUTLET TEMPERATURE    F                                    194.00
OUTLET PRESSURE       PSI                                  870.23
HEAT DUTY             BTU/HR                            -0.12221E+08
VAPOR FRACTION                                           0.0078634

REACTION EXTENTS:

   REACTION          REACTION
   NUMBER            EXTENT
                     LBMOL/HR
      1               130.98
      2               1.9946
```

V-L PHASE EQUILIBRIUM :

COMP	F(I)	X(I)	Y(I)	K(I)
CO	0.073365	0.066304	0.96419	14.542
PROPANE	0.00012129	0.00012186	0.000049108	0.40299
PD	0.0078727	0.0079130	0.0027904	0.35264
MEOH	0.38613	0.38899	0.025126	0.064593
MMA	0.52298	0.52707	0.0078166	0.014830
MC	0.0070789	0.0071348	0.000025625	0.0035916
ACID	0.0022751	0.0022931	0.10305E-08	0.44938E-06
P-MET-01	0.00017693	0.00017833	0.28713E-08	0.000016101

BLOCK: T550 MODEL: FLASH2

```
INLET STREAM:                490
OUTLET VAPOR STREAM:         550
OUTLET LIQUID STREAM:        595
PROPERTY OPTION SET:         UNIQUAC   UNIQUAC / IDEAL GAS

                      ***  MASS AND ENERGY BALANCE  ***
                                   IN                OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)              327.490           327.490          0.0
    MASS(LB/HR    )             22289.6           22289.6          0.231813E-10
    ENTHALPY(BTU/HR  )      -0.424648E+08     -0.382633E+08     -0.0989424

                          ***  INPUT DATA  ***
 TWO    PHASE  TP  FLASH
 SPECIFIED TEMPERATURE F                                        194.000
 SPECIFIED PRESSURE    PSI                                       16.7900
 MAXIMUM NO. ITERATIONS                                          30
 CONVERGENCE TOLERANCE                                           0.00010000

                            ***  RESULTS  ***
 OUTLET TEMPERATURE    F                                         194.00
 OUTLET PRESSURE       PSI                                       16.790
 HEAT DUTY             BTU/HR                                   0.42016E+07
 VAPOR FRACTION                                                  0.97668

 V-L PHASE EQUILIBRIUM :

    COMP            F(I)          X(I)          Y(I)          K(I)
    CO            0.073365    0.000099646     0.075114      753.80
    PROPANE      0.00012129   0.45394E-05     0.00012408     27.333
    PD           0.0078728    0.00036635      0.0080520      21.979
    MEOH          0.38612      0.086317        0.39328        4.5564
    MMA           0.52299      0.78791         0.51666        0.65574
    MC           0.0070789     0.020733        0.0067529      0.32571
    ACID         0.0022751     0.097425       0.32154E-05     0.000033004
    P-MET-01     0.00017694    0.0071484       0.000010486    0.0014670
```

BLOCK: V495 MODEL: VALVE

```
INLET STREAM:                 450
OUTLET STREAM:                490
PROPERTY OPTION SET:          UNIQUAC   UNIQUAC / IDEAL GAS

                        ***  MASS AND ENERGY BALANCE  ***
                                      IN                    OUT          RELATIVE DIFF.
 TOTAL BALANCE
    MOLE(LBMOL/HR)                  327.490               327.490          0.0
    MASS(LB/HR    )                 22289.6               22289.6          0.326428E-15
    ENTHALPY(BTU/HR   )         -0.424648E+08         -0.424648E+08        -0.350906E-15

                                 ***  INPUT DATA  ***

VALVE OUTLET PRESSURE       PSI                                            16.7900
VALVE FLOW COEF CALC.                                                      NO

                                 FLASH SPECIFICATIONS:

NPHASE                                                                      2
MAX NUMBER OF ITERATIONS                                                   30
CONVERGENCE TOLERANCE                                                       0.00010000

                                 ***  RESULTS  ***

VALVE PRESSURE DROP         PSI                                           853.436
```

STORAGE VESSEL COSTING

	C3 Feed 1 day	C3 Byproduct 1 day	MSA 30 days	Phosphine 30 days	Inhibitor 30 days	Inhibitor Mixer/Melter
Volume (gal)[32]	68,617	45,641	1430	6064	120	28.90
Volume (cuft)[32]	9,173	6,101	191	811	16	3.686
Diameter (ft) [29]	15.73	13.73	4.33	7.01	1.90	1.31
Diameter (ft)	15	13	4	7	1	1
Diameter (in)	9	9	4	0	11	4
Height (ft)	47.19	41.20	12.98	21.02	5.69	5.25
Height (ft)	47	41	12	21	5	5
Height (in)	2	2	12	0	8	3
Aspect Ratio [L/D]	3	3	3	3	3	4
Spec. Vol (cuft)	9173	6101	191	811	16.10	7.09
Sum Lin. Ft	63	55	17	28	8	7
Volume (m^3)[25]	260	173	5	23	0.4559	0.1044
Pressure (barg)[32]	11.05	11.05	0	0	0	1
Cp [26]	$90,000	$65,000	$1,800	$4,000	$700	$700
MOC	cs	cs	cs-gl	cs	cs	cs
FBM [26]	2.1	2.1	5.4	1.9	1.9	1.9
CBM 1982 [26]	**$189,000**	**$136,500**	**$9,720**	**$7,600**	**$1,330**	**$1,330**
CBM 1999 [31]	**$240,000**	**$174,000**	**$13,000**	**$10,000**	**$2,000**	**$2,000**
type from Ulrich fig :	bullet	bullet	cone roof	cone roof	hopper bin	tank
oversized by			1.5	1.5	1.5	

	Pd(II)Acetate 30 days	MMA Product 30 days	Catalyst Waste 30 days	Catalyst Mixer	MeOH 7 days	Total
Volume (gal) [32]	20.5	1,286,434	8.9	11.25	118,463	
Volume (cuft) [32]	3	171,972	1.19	1.52	15,836.30	
Diameter (ft) [29]	1.08	41.79	0.80	0.86	18.87	
Diameter (ft)	1	41	0	0	18	
Diameter (in)	1	9	10	10	10	
Height (ft)	3.25	125.37	2.39	2.59	56.62	
Height (ft)	3	125	2	2	56	
Height (in)	3	4	5	7	7	
Aspect Ratio [L/D]	3	3	3	3	3	
Spec. Vol (cuft)	3.00	171,972	1.19	1.52	15,836	
Sum Lin. Ft	4	167	3	3.46	75	
Volume (m^3) [25]	0.078	4870	0.034	0.000	448	
Pressure (barg)[32]	0	0	0	0	0	
Cp [26]	$700	$80,000	$700	$700	$16,000	
MOC	cs	cs	cs-gl	cs-gl	cs	
FBM [26]	1.9	1.9	5.4	5.4	1.9	
CBM 1982 [26]	**$1,330**	**$152,000**	**$3,780**	**$3,780**	**$30,400**	**$536,770**
CBM 1999 [31]	**$2,000**	**$194,000**	**$5,000**	**$5,000**	**$39,000**	**$682,000**
type from Ulrich fig :	hopper bin	cone roof	cone roof	cone roof	cone roof	
oversized by	1.5	1	1.5			

Pump Costing

(correlations Ulrich)	Extractive Distillate Pump	Reactor Reflux Pump	Azeotropic Reflux Pump	Crotonate Removal Reflux Pump	Inhibitor - Reactor Pump
Shaft Power (kW) [18]	0.75	10.70	0.75	0.75	0.745000
Pressure (psi) [32]	15.7	870	22	15	15
Pressure (barg) [32]	0.08	58.98	0.52	0.03	0.03
Material (MOC)	C Steel	Hastelloy-C	Hastelloy-C	Hastelloy-C	C Steel
Cp [19]	$1,500	$21,000	$1,500	$1,500	$1,500
Fp [19]	1.00	2.10	1.00	1.00	1.00
Fm [19]	1.4	9	1.4	1.4	1.4
FBM [19]	4	30.5	4	4	4
CBM [19]	$6,000	$641,000	$6,000	$6,000	$6,000
Spare Factor	2	2	2	2	2
Pump Type	Centrif., SS, SS	Recip, Mult Plunger	Rotary, Screw	Rotary, Screw	Rotary, Horz Inline
ΔP (lbf/sqft) [32]	1440	1,598.40	1,440.00	39,129.51	1440
Volumetric Flow Rate (cuft/s)[32]	0.07	2.48	0.15	0.16	0.000002
Efficiency (ε) [32]	0.8	0.5	0.8	0.8	0.8
CBM (total) 1982 [19]	**$12,000**	**$1,282,000**	**$12,000**	**$12,000**	**$12,000**
CBM (total) 1999 [31]	**$16,000**	**$1,628,000**	**$16,000**	**$16,000**	**$16,000**

Pump Costing

(correlations Ulrich)	Azeotropic Bottoms Pump	Azeotropic Distillate Pump	Crotonate Removal Bottoms Pump	Crotonate Removal Distillate Pump	Extractive Reflux Pump
Shaft Power (kW) [18]	0.075	0.745	0.745	0.745	0.75
Pressure (psi) [32]	23	22	23.4	14.7	14.7
Pressure (barg) [32]	0.59	0.52	0.61	0.01	0.01
Material (MOC)	C Steel	C Steel	C Steel	C Steel	C Steel
Cp [19]	$1,900	$1,500	$1,500	$1,500	$1,500
Fp [19]	1.00	1.00	1.00	1.00	1.00
Fm [19]	1.4	1.4	1.4	1.4	1.4
FBM [19]	4	4	4	4	4
CBM [19]	$8,000	$6,000	$6,000	$6,000	$6,000
Spare Factor	2	2	2	2	2
Pump Type	Centrifugal	Recip, Metering Plunger	Centrifugal Multistage	Recip Metering Plunger	Rotary, Gear
ΔP (lbf/sqft) [32]	-			-	1,440.00
Volumetric Flow Rate (cuft/s) [32]	-	-	-	-	0.28
Efficiency (ε) [32]	-	-	-	-	0.8
CBM (total) 1982 [19]	**$16,000**	**$12,000**	**$12,000**	**$12,000**	**$12,000**
CBM (total) 1999 [31]	**$21,000**	**$16,000**	**$16,000**	**$16,000**	**$16,000**

Pump Costing

(correlations Ulrich)	C_3 Feed Pump	Catalyst Reactor Feed Pump	Extractive Bottoms Pump	Methanol Extractive Pump
Shaft Power (kW) [18]	7.2	2.02	32.4	8.01
Pressure (psi) [32]	175	25	262.9	25
Pressure (barg) [32]	11.07	0.72	17.13	0.72
Material (MOC)	C Steel	Hastelloy-C	C Steel	C Steel
Cp [19]	$9,000	$10,000	$17,000	$6,000
Fp [19]	1.10	1.00	1.25	1.00
Fm [19]	1.4	9	1.4	1.4
FBM [19]	5	15.5	4.5	4
CBM [19]	$45,000	$155,000	$77,000	$24,000
Spare Factor	2	2	2	2
Pump Type	Centrifugal	Recip, Metering Plunger	Rotary, Gear	Centrifugal
ΔP (lbf/sqft) [32]	Single Stage	-	-	Single Stage
Volumetric Flow Rate (cuft/s) [32]	Single Suction	-	-	Single Suction
Efficiency (ε) [32]	-	-	-	-
CBM (total) 1982 [19]	**$90,000**	**$310,000**	**$154,000**	**$48,000**
CBM (total) 1999 [31]	**$115,000**	**$394,000**	**$196,000**	**$61,000**

Pump Costing

(correlations Ulrich)	Inhibitor - Azeotropic Pump	Inhibitor - Crotonate Pump
Shaft Power (kW) [18]	0.745000	0.745000
Pressure (psi) [32]	15	15
Pressure (barg) [32]	0.03	0.03
Material (MOC)	C Steel	C Steel
Cp [19]	$1,500	$1,500
Fp [19]	1.00	1.00
Fm [19]	1.4	1.4
FBM [19]	4	4
CBM [19]	$6,000	$6,000
Spare Factor	2	2
Pump Type	Process, Horz. Inline	Process Horz. Inline
ΔP (lbf/sqft) [32]	1440	1440
Volumetric Flow Rate (cuft/s)[32]	0.0000013	0.0000009
Efficiency (ε) [32]	0.8	0.8
CBM (total) 1982 [19]	**$12,000**	**$12,000**
CBM (total) 1999 [31]	**$16,000**	**$16,000**

Pump Costing

(correlations Ulrich)	Catalyst Batch Pump	Methanol Feed Pump
Shaft Power (kW) [18]	0.7450	0.745
Pressure (psi) [32]	15	25
Pressure (barg) [32]	0.03	0.72
Material (MOC)	Hastelloy-C	C Steel
Cp [19]	$1,500	$1,500
Fp [19]	1.00	1.00
Fm [19]	9	1.4
FBM [19]	15.5	4
CBM [19]	$24,000	$6,000
Spare Factor	2	2
Pump Type	Recip, Metering Diaph	Reciprocating
ΔP (lbf/sqft) [32]	1440	Metering
Volumetric Flow Rate (cuft/s)[32]	0.0011	Plunger Pump
Efficiency (ε) [32]	0.8	-
CBM (total) 1982 [19]	**$48,000**	**$12,000**
CBM (total) 1999 [31]	**$61,000**	**$16,000**

Vessel Costing

(correlations Ulrich)	Extractive Reflux Tank	Crotonate Removal Reflux Tank	Azeotropic Reflux Tank	Flash Tank
Diameter (m) [32]	2.10	1.54	1.32	1.18
Height (m) [29]	6.29	4.62	3.29	3.54
Pressure (barg) [32]	16.09	0.0325	0.0325	0.2058
Vol Flow (cuft/min) [32]	76.52	30.41	15.84	1059.53
Hold Up Time (min)	5	5	5	10
Volume (m3) [22]	21.68	8.61	4.49	300.15
Spec. Volume (m3)	21.68	8.61	4.49	3.89
L/D	3.00	3.00	2.5	2.5
FBM [3]	4.5	3.3	3.3	13.5
FM [3]	1	1	1	5.5
Fp [3]	2	1.2	1.2	1.2
Material (MOC)	Carbon Steel	Carbon Steel	Carbon Steel	HC lining/CS shell
Cp [3]	$16,000	$17,000	$10,000	$6,000
CBM (1982) [3]	**$70,000**	**$53,000**	**$33,000**	**$81,000**
CBM (1999) [31]	**$89,000**	**$68,000**	**$42,000**	**$103,000**
Superficial Velocity (m/s) [23]	-	-	-	1.144761573
Liquid Density (lb/cuft) [32]	-	-	-	54.56
Gas Density (lb/cuft) [32]	-	-	-	0.17

Column Costing

(correlations Ulrich)	Extractive (2 columns)	Crotonate Removal	Azeotropic
Tray Spacing (in) [32]	20	20	20
Diameter (m) [32]	1.43	1.45	1.71
Height per column (m) [32]	39.63	47.76	8.64
No. Trays [32]	105	61	8
Actual No. Trays [2]	150	88	11
Pressure (barg) [32]	16.099	0.0325	0.0325
FBM [3]	6	7.8	4.5
fq [4]	1	1	2
FM [3]	1	2.5	1
Tray Efficiency (%) [32]	0.7	0.7	0.7
Fp [3]	2	1.2	1.2
CBM (sieve) [4]	$220,000	$168,000	$28,000
CBM (column) [3]	$217,000	$577,000	$103,000
CBM (Total Column) 1982	**$437,000**	**$745,000**	**$131,000**
CBM (Total Column) 1999 [31]	**$555,000**	**$947,000**	**$167,000**
Cp (Total) [3]	$73,000	$96,000	$30,000
Material (MOC)	Carbon Steel	Stainless Steel clad	Carbon Steel
CBM TOTAL (with Reflux Tanks) 1982	**$507,000**	**$798,000**	**$164,000**
CBM TOTAL (Refl, Reboil,Cond) 1999	**$768,000**	**$1,260,000**	**$366,000**
CBM (Col, Reflux, Reboil & Cond) 1982	$604,000	$991,000	$287,000

Heat Exchanger Costing

(correlations Ulrich)	Pre-Reaction Heat Exchanger	Reactor Heat Exchanger	Extractive Condenser
Pressure (barg) [32]	58.98	59	-
SA (sqft) [7]	99.44	1048.13	1416.93
SA (sqm) [7]	9.24	97.37	131.64
FBM [17]	3.3	14.5	3.3
FM [17]	1	7.2	1
Fp [17]	1.1	1.1	1
Material (MOC)	Carbon Steel	Hastelloy-C Tubes/ CS Shell	Carbon Steel
Cp [17]	$4,000	$10,250	$11,000
Q (Btu/hr) [32]	1,640,684	12,553,992	5,251,850
ΔTLM (°F) [32]	110.0	79.9	24.71
U (Btu/hr °F sqft) [32]	150	150	150
CBM 1982 [17]	**$14,000**	**$149,000**	**$37,000**
CBM 1999 [31]	**$18,000**	**$190,000**	**$47,000**

(correlations Ulrich)	Crotonate Removal Condenser	Crotonate Removal Reboiler	Azeotropic Condenser
Pressure (barg) [32]	-	-	-
SA (sqft) [27]	7055.63	613.64	2839.47
SA (sqm) [27]	655.49	57.01	263.80
FBM [3]	3.3	4.5	3.3
FM [3]	1	1.7	1
Fp [3]	1.1	1.1	1.1
Material (MOC)	Carbon Steel	Stainless Steel	Carbon Steel
Cp [3]	$35,000	$17,000	$18,000
Q (Btu/hr) [32]	6,307,730	6,136,360	13,782,808
ΔT (°F) [32]	6	-	32.36
U (Btu/hr °F sqft) [32]	150	150	150
CBM 1982 [17]	**$116,000**	**$77,000**	**$60,000**
CBM 1999 [31]	**$148,000**	**$98,000**	**$77,000**

Heat Exchanger Costing

(correlations Ulrich)	Extractive Reboiler
Pressure (barg) [32]	-
SA (sqft) [27]	810.91
SA (sqm) [27]	75.34
FBM [17]	3.3
FM [17]	1
Fp [17]	1
Material (MOC)	Carbon Steel
Cp [17]	$18,000
Q (Btu/hr) [32]	8,109,140
ΔTLM (°F) [32]	-
U (Btu/hr °F sqft) [32]	150
CBM 1982 [17]	**$60,000**
CBM 1999 [31]	**$77,000**

(correlations Ulrich)	Azeotropic Reboiler
Pressure (barg) [32]	-
SA (sqft) [27]	878.67
SA (sqm) [27]	81.63
FBM [17]	3.3
FM [17]	1
Fp [17]	1.1
Material (MOC)	Carbon Steel
Cp [17]	$19,000
Q (Btu/hr) [32]	8,786,660
ΔT (°F) [32]	-
U (Btu/hr °F sqft) [32]	150
CBM 1982 [17]	**$63,000**
CBM 1999 [31]	**$80,000**

Reactor Costing

(correlations Ulrich)	Isomerization
Pressure (barg) [32]	16.2
Spare Factor	2
SA (sqm) [27]	209.87
FBM [17]	3.3
FM [17]	1
Fp [17]	1.05
Material (MOC)	Carbon Steel
Cp [17]	$40,000
CBM 1982 [17]	**$132,000**
CBM 1999 [31]	**$168,000**

Reactor Vessel Costing

(correlations Ulrich)	Carboxymethylation
Diameter (m) [32]	1.88
Height (m) [29]	4.69
Pressure (barg) [32]	58.98
Vol Flow (cuft/min) [32]	7.63
Hold Up Time (min)	60
Volume (m3) [28]	12.97
Spec. Volume (m3)	12.97
L/D	2.50
FBM [3]	19
FM [3]	10
Material (MOC)	Hastelloy-C
Cp [3]	$42,000
CBM 1982 [3]	**$795,000**
CBM 1999 [31]	**$1,010,000**

Blower Costing

Blower/Compressor

Power (kW) [32]	124
FBM [19]	2.2
Material	Carbon Steel
Type	Rotary
CBM 1982 [20]	**$359,000**
CBM 1999 [31]	**$456,000**
Spare Factor	2

G. Patents

US005081286A

United States Patent [19]

Doyle et al.

[11] **Patent Number: 5,081,286**

[45] **Date of Patent: Jan. 14, 1992**

[54] **PROCESS FOR THE PREPARATION OF AN ALKYL METHACRYLATE**

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[52] **U.S. Cl.** **560/206; 560/207; 562/522**
[58] **Field of Search** 560/206, 207; 502/522

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[57] **ABSTRACT**

A process for the preparation of an alkyl methacrylate, which process comprises:

a) selectively removing propadiene from a C_3-mixture comprising a mixture of propyne and propadiene that has been obtained from an ethene cracker, a catalytic cracker or an LPG-dehydrogenation process, to provide a propyne feed in which the ratio of propyne to propadiene is at least about 6:1, nd

b) contacting the propyene feed with carbon monoxide and an alkanol in the presence of a carboxylation catalyst.

25 Claims, No Drawings

PROCESS FOR THE PREPARATION OF AN ALKYL METHACRYLATE

BACKGROUND OF THE INVENTION

The present invention relates to a process for the preparation of an alkyl methacrylate. In a specific aspect, the invention relates to a process for preparing methyl methacrylate.

Methyl methacrylate is prepared in industry mainly by the acetone cyanohydrin process. This process presents disadvantages in that large quantities of waste sulphuric acid and ammonium bisulphate are produced, and these by-products must be discharged or worked up for reuse. Another by-product, HCN, is highly toxic and raises difficult problems of storage and transportion. As concerns about the environment have increased, considerable research has been devoted to finding alternative processes which do not present these disadvantages.

One possible alternative process, described in 1964 by Y. Sakakibira in Bull. Chem. Soc. Japan 37, 11 (1964) 1601–1609, involves the reaction of propyne with carbon monoxide and alkanol in the presence of a carboxylation catalyst. Although this process has been known for a long time and has attracted a considerable amount of interest, it has never been commercialized.

A factor inhibiting the commercial exploitation of the carboxylation process has been the unavailability of large quantities of a suitable low-priced propyne feed.

Many processes have been described for the preparation of propyne. For example, the chapter "Methylacetylene" in Kirk-Othmer's Encyclopedia of Chemical Technology, 2nd ed., Volume Supplement (1971), pages 547 to 556, refers to various processes including the dehydrohalogenation of propylene dibromide, the hydration of magnesium carbide, the reaction of sodium acetylide and dimethylsulphate in liquid ammonia, and a variety of pyrolysis or cracking methods.

European patent application publication number EP-A-0190473 discloses a process for the preparation of alkyl acrylates, such as methyl methacrylate, by the carboxylation of propadiene. Example 10 in the specification describes an experiment in which methyl methacrylate is prepared by reacting a mixture of propadiene and propyne with carbon monoxide and methanol in the presence of a relatively inactive carboxylation catalyst. Both the propadiene and the propyne are converted into methyl methacrylate. Surprisingly, it has now been found that propadiene poisons carboxylation catalysts in the carboxylation of propyne and methanol to give methyl methacrylate. Moreover, the poisoning effect of propadiene appears to increase as the intrinsic activity of the carboxylation catalyst for propyne carboxylation increases.

It is thus an object of the invention to provide a process for the preparation of an alkyl methacrylate which can be carried out at industrial scale and at low cost. It is a further object of the invention to provide a process which uses large quantities of propyne in a quality in which it may be easily supplied. Finally, it is an object of the invention to provide an industrial scale process which can make use of high activity carboxylation catalysts.

SUMMARY OF THE INVENTION

Accordingly, the invention provides a process for the preparation of an alkyl methacrylate, which comprises:

a) selectively removing propadiene from a C_3 mixture comprising a mixture of propyne and propadiene that has been obtained from an ethene cracker, a catalytic cracker or an LPG-dehydrogenation process, to afford a propyne feed in which the ratio of propyne to propadiene is at least about 6:1, and b) contacting the thus-treated propyne feed with carbon monoxide and an alkanol in the presence of a carboxylation catalyst.

DETAILED DESCRIPTION OF THE INVENTION

Of the many potential sources of a propyne feed for the preparation of alkyl methacrylates, the cheapest appears to be the C_3-stream produced by an ethene cracker (also known as a naphtha cracker, a gas oil cracker and/or an LPG cracker), a catalytic cracker or an LPG (liquefied petroleum gas)-dehydrogenation process. A characteristic of such a stream is that it comprises a mixture of propyne and propadiene in an approximate ratio of 1 to 1. At present, the mixture of propyne and propadiene is generally not separated, but is usually burned (either as a flare or as welding gas) or is hydrogenated to propene and propane.

The C_3-mixture used as the starting material in the process according to the invention is a by-product stream from an ethene cracker, a catalytic cracker or an LPG-dehydrogenation process which comprises a mixture of propyne and propadiene. Ethene crackers, catalytic crackers and LPG-dehydrogenation processes are well known.

An ethene cracker is a type of cracker in which ethene is prepared from hydrocarbon fractions such as naphtha, gas oil, LPG (preferably isobutane) or ethane by thermal cracking. A catalytic cracker is a cracker in which hydrocarbons are prepared by the catalytic cracking of hydrocarbon fractions such as heavy gas oil or vacuum distillates. An LPG-dehydrogenation process is a process in which propane is converted into propene, either thermally or catalytically. Each of these processes provides, among others, a C_3-stream consisting mainly of C_3-hydrocarbons, in particular propane, propene, propyne and propadiene. Preferably the C_3-mixture comprises a mixture of propyne and propadiene that has been obtained from an ethene cracker.

The C_3-mixture used in the process according to the invention may be a C_3-stream produced by an ethene cracker, a catalytic cracker or an LPG-dehydrogenation process. However, it is preferably a mixture derived from a C_3-stream by a process in which the concentration of the mixture of propyne and propadiene has been increased. For example, it may be a mixture derived from such a C_3-stream by distilling-off propane and/or propene, by selective scrubbing with a solvent and/or by adding more propyne and/or propadiene. More propyne and/or propadiene may be added, for example by way of a recycle to be described in greater detail hereinafter.

In some cases, it will be very convenient to combine mixtures of propyne and propadiene obtained from several different ethene crackers, catalytic crackers and/or LPG-dehydrogenation processes, which may be located at different refineries. Such mixtures will most conveniently be transported in concentrated form.

An attractive way of obtaining the C_3-mixture from an ethene cracker plant comprises taking at least part of the "crude" C_3-stream obtained from an already present depropaniser (a distillation column in which C_3-hydro-

carbons are separated from higher hydrocarbons), bypassing the hydrogenator (where normally the propyne, propadiene and some propene are hydrogenated to a propane/propene mixture, whence the latter mixture is fed to a propane/propene splitter from which "polymer grade" propene is obtained as a top stream and essentially pure propane as a bottom stream) and introducing it directly into a propane/propene splitter. In this embodiment, it is advantageous to operate the splitter under slightly different conditions than when operating with hydrogenation as described above, to account for the fact that at least part of its feed still contains some propyne and/or propadiene, as it has not been subjected to a preliminary hydrogenation. It would then be operated such that the top stream of the splitter would still contain "polymer grade" propene, though in lesser yield, and some of the propene would leave the splitter at the bottom with a stream which consists mainly of propane and propene (about 70%) and further contains propadiene and propyne in roughly equimolar portions.

It is advantageous to minimize the amount of inert or quasi-inert materials in the propyne feed in order to maximize the throughput of a plant having a fixed capacity at a given catalyst activity. Thus, according to a preferred aspect of the invention, the mixture of propyne and propadiene in the C_3-mixture can be concentrated by selective scrubbing with a solvent, whereby a solvent stream containing the C_3-mixture is obtained. For example, the mixture of propyne and propadiene may have been obtained from the bottom effluenet of a propane/propene splitter which contains significant amounts of propane, propene, propyne and propadiene. The scrubbing is suitably carried out in a column under elevated pressure (2–20, preferably 6–12 bar) using countercurrent flows of an organic solvent and the bottom effluent of the propane/propene splitter, so that typically a stream consisting essentially of propane and propene (and <0.2% of propyne/propadiene) is removed as the overhead fraction.

The solvent which absorbs propyne and also propadiene at the elevated pressure employed, suitably comprises a polar organic solvent, such as an amide, e.g. dimethylformamide, dimethylacetamide or N-methylpyrrolidone; a nitrile such as acetonitrile; a sulfone such as sulfolane; or a mixture thereof. Dimethylformamide is particularly suitable. Another preferred extraction solvent is an alcohol such as methanol, which presents the advantage that it can be used as one of the reactants in the subsequent carboxylation reaction, and thus simplifies the management of the process.

The propadiene may be selectively removed by chemical means, such as by isomerization to propyne, and/or by physical means such as by distillation, preferably extractive distillation.

The isomerization of propadiene into propyne is a chemical equilibrium reaction and is well known in the art. The position of chemical equilibrium depends upon the temperature. Thus as the temperature is increased, the proportion of propadiene increases. At ambient temperature, the ratio of propyne to propadiene obtained by isomerization is approximately 9 to 1.

The isomerization is conveniently effected in the gas or liquid phase in the presence of an isomerization catalyst at a temperature in the range of from about −30° to about 100° C., preferably about 0° to about 40° C., more preferably about 10° to about 30° C., and at a pressure in the range from about 0.1 to about 100 bar, more preferably about 1 to about 20 bar.

Catalysts suitable for isomerizing propadiene into propyne are well known. For example, the isomerization catalyst may comprise an alkali metal or alkali metal oxide deposited on alumina, such as a composition obtainable by heating an alkali metal carbonate deposited on an alumina carrier, preferably K_2CO_3 on gamma alumina, in an inert atmosphere, or a composition obtainable by depositing at least one molten alkali metal on alumina, preferably the low melting eutectic mixture of potassium and sodium on alumina. Suitable isomerization catalyts are also described in Kirk-Othmer's Encyclopaedia of Chemical Technology, 2nd ed., Volume Supplement (1971), pages 547 to 556, and in U.S. Pat. No. 3,671,605.

In general, the activity of isomerization catalysts decreases with decreasing temperature. Accordingly, when it is desired to prepare a propyne feed in which the ratio of propyne to propadiene is ≧10, especially ≧20, it is preferable to remove propadiene from the C_3-mixture by physical separation means.

When propadiene has been removed by physical separation means it may then be reacted with carbon monoxide and an alkanol to afford alkyl methacrylate. However, it is preferably isomerized to a mixture of propyne and propadiene, and recycled to step a) or step b) of the process. Optionally, the product of the isomerization is subjected to a distillation to remove heavy ends prior to recycling to step a) or step b).

Extractive distillation is a method well known for removing one component from a mixture comprising two very similar components. Thus, for the removal of propadiene from a mixture of propyne and propadiene, the mixture of propyne and propadiene is dissolved in a polar organic solvent, and propadiene is removed as a gas (e.g. by stripping) leaving propyne dissolved in the solvent. Suitable solvents include amides, for example dimethyl formamide or N-methylpyrrolidone, nitriles such as acetonitrile, sulfones such as sulfolane and alcohols such as methanol. Dimethylformamide, N-methylpyrrolidone, methanol and mixtures thereof are preferred solvents.

It will be appreciated that by combining a physical separation step for the removal of propadiene with an isomerization step, all of the propyne and propadiene in the original C_3-mixture can in principle be converted into alkyl methacrylate. This combination of process steps therefore constitutes a particularly preferred aspect of the invention.

When the C_3-mixture has been obtained by scrubbing with a solvent, propadiene is advantageously removed by stripping from the propyne and propadiene containing solvent stream to afford the propyne feed. This stripping is possible because propadiene and propyne exhibit different volatilities and solubilities in solvents. The stripping may suitably take place in a column downstream of the main absorption column, employing indirect heat exchange in the bottom of the column. The propyne may then, if desired, be separated from the solvent in a further column. The stripping operation can be adjusted to a propadiene content in the propyne feed of almost zero.

In the process according to the invention, the molar concentration of propyne in the propyne feed preferably lies above about 35%, more preferably above about 50%, even more preferably above about 90%, most preferably at least about 99%. Thus the feed mixture preferably contains at most about 10% (molar) of propadiene and at least about 35% (molar) of propyne.

The propene feed preferably comprises at least about 50% (mass) of propyne and propadiene combined, more preferably at least about 60%, even more preferably at least about 80%. The propyne feed preferably comprises at least about 50%, especially at least about 90% (molar), of C_3-hydrocarbons.

In the process according to the invention, it is preferred to use a propyne feed in which the ratio of propyne to propadiene is at least about 8, particularly ≧20, and especially ≧100. With highly active carboxylation catalysts, it is preferable to use a propyne feed in which the ratio is ≧500, more preferably ≧1000, most preferably ≧10,000.

The carboxylation catalyst used in the process according to the invention may be any catalyst having activity for the carboxylation of propyne. It is preferably a Group VIII metal catalyst, more preferably a palladium catalyst.

Preferably the carboxylation catalyst is based on a composition of a Group VIII (e.g. palladium) compound, a ligand (e.g. a monodentate or quasi-bidentate phosphine, arsine, stibine or a similar nitrogen compound) and an anion of a Broensted acid (from a salt, ester, anhydride or acid, and preferably not too strongly coordinating). A particularly preferred example of such a catalyst is based on a composition of a palladium (II) compound, an organic phosphine of formula PR_3 in which each R independently stands for an optionally substituted hydrocarbyl or heterocyclic group, and a non-hydrohalogenic Broensted acid having a $pK_A < 2$.

A hydrocarbyl group in an optionally substituted hydrocarbyl group is preferably an alkyl group, for example a C_{1-6} alkyl group such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, or t-butyl, a cycloalkyl group, e.g. cyclopentyl or cyclohexyl, or an aryl group such as phenyl or naphthyl. Two R-groups may alternatively represent an optionally substituted alkylene chain.

A heterocyclic group in an optionally substituted heterocyclic group is preferably an aromatic group having an imino nitrogen, for example a pyridyl, pyrazinyl, quinolyl, isoquinolyl, pyrimidinyl, pyridazinyl, cinnolinyl, triazinyl, quinoxalinyl or quinazolinyl group. An imino nitrogen atom in an aromatic group having an imino nitrogen atom is preferably connected to phosphorus through a single bridging nitrogen atom, as for example in 2-pyridyl, 2-pyrazinyl, 2-quinolyl, I-isoquinolyl, 3-isoquinolyl, 2-pyrimidinyl, 3-pyridazinyl, 3-cinnolinyl, 2-triazinly, 2-quinoxalinyl and 2-quinazolinyl.

Examples of optional substituents which may be present in an optionally substituted hydrocarbyl or heterocyclic group include halogen atoms, e.g. fluorine, chlorine or bromine; alkyl groups, i.e. methyl or ethyl; haloalkyl groups, e.g. trifluoromethyl; alkoxy groups, e.g. methoxy or ethoxy; haloalkoxy groups, e.g. trifluoromethoxy; acyl groups, e.g. acetyl; acyloxy groups, e.g. acetoxy; amino groups, e.g. dimethylamino; hydroxyl groups; nitrile groups; acylamino groups, e.g. acetamido; and aryl groups, e.g. phenyl.

A non-halogenic Broensted acid may be, for example, sulfuric acid, a sulfonic acid such as p-toluenesulfonic acid, naphthalenesulfonic acid, trifluoromethanesulfonic acid, chlorosulfonic acid, fluorosulfonic acid or a sulfonated ion exchange resin; a phosphoric acid such as orthophosphoric acid, pyrophosphoric acid or benzene phosphoric acid; a carboxylic acid such as trifluoroacetic acid; a perhalic acid such as perchloric acid; fluorosilicic acid; HBF_4; HPF_6 or $HSbF_6$.

Examples of such catalysts are mentioned in U.S. Pat. No. 4,739,109, the disclosure of which is incorporated herein by reference. Most preferable examples include combinations of (a) palladium acetate, (b) triphenylphosphine, tris(p-methoxyphenyl)phosphine, or diphenyl-2-pyridylphosphine, and (c) p-toluenesulfonic or trifluoroacetic acid.

The reaction between propyne, the alcohol and carbon monoxide is preferably effected at a temperature in the range of from about 20° to about 200° C., more preferably about 20° to about 80° C., and at a pressure in the range of from about 5 to about 70 bar. A separate solvent is not essential for the reaction. However, an ester of the alcohol may conveniently be used as solvent.

When the carboxylation catalyst is a Group VIII metal catalyst, it is preferred that the catalyst has a conversion activity in the absence of propadiene of at least about 100 g propyne/g of catalytic metal/hour, more preferably about 1,000 g propyne/g of catalytic metal/hour, preferably of at least about 5,000, more preferably of at least about 10,000 g propyne/g of catalytic metal/hour. This is equivalent roughly to a production of about 25 kg methacrylate/g catalytic metal/hour, where the catalytic metal is palladium and the methacrylate is methyl methacrylate.

The alkyl methacrylate which is the product of the present process is suitably an ester of an alcohol having up to 20, preferably 1 to 4 carbon atoms. Examples of alcohols are methanol, ethanol, propanol, iso-propanol, butanol, iso-butanol and tert-butanol. Most preferably the alkanol is methanol, thus giving methyl methacrylate as the product.

A suitable and attractive method for carrying out the carboxylation reaction involves combining the propyne feed with a mixture of fresh alkanol and a recycle stream of an methacrylate/alkanol azeotrope, and then feeding this combined feed stream into the reactor simultaneously with (a solution of) the catalyst and carbon monoxide.

This process is further described using methanol as the preferred alkanol feed. Very suitably the propyne feed is brought into a mixing device, e.g. tank, to combine it with a mixture of fresh methanol and a recycle stream of a methyl methacrylate/methanol azeotrope, and is then fed into the reactor, and concomitant with that, the catalyst solution is also fed into the reactor. One could introduce the catalyst solution using the CO feed pipe or separately. The reactor effluent product stream is flashed isothermally and stripped of unreacted gases. This gas steam may be chilled (to about −20° C.) to recondensed valuable low volatile components which are returned to the liquid feed. The uncondensed gas (mainly CO) is removed and used elsewhere, e.g. as a fuel. Any unreacted propyne present therein can be scrubbed out with methanol and recycled to the reactor. The liquid fraction, which contains product, catalyst residues and heavy ends, is fed into a distillation column.

The column top stream, which consists of an azeotrope of methyl methacrylate and methanol, is recycled to the feed mixing device and subsequently to the reactor. The bottom stream is suitably fed to a second distillation column. The top product from this column is pure methyl methacrylate, whereas the bottom product contains some methacrylate, catalyst residues and

heavy ends. The latter methyl methacrylate may be recovered in a heavy ends stripper and returned to the second column. The concentrated residue may be worked up for reuse or for disposal in a responsible way.

The invention will now be illustrated in more detail by the following Examples. Example 1 illustrates a process in which a C_3-mixture typical of that of a C_3-steam from a cracker is converted into a propyne feed by scrubbing with a solvent followed by stripping off of propadiene. Example 2 illustrates a process in which propadiene is isomerized over an isomerization catalyst to afford propyne. Examples 3 and 4 illustrate the carboxylation of proyne to afford methyl methacrylate. The Comparative Examples demonstrate the poisoning effect of propadiene on the carboxylation of propyne.

EXAMPLE 1

In a calculated experiment, a fresh feed, consisting of 52.7 mole % propane, 1.6 mole % of propylene, 19.1 mole % of propadiene and 25.1 mole % of propyne and 1.5% of heavier hydrocarbons, is combined with a recycle stream from a propadiene isomerization reactor and fed to an absorption column. If necessary the feed is first sent to a distillation column to remove high boiling impurities. The combined mixture contains 45.4% propane, 10.5% propylene, 11.4% propadiene and 32.7% propyne.

In the absorber the combined mixture is contacted with DMF (dimethylformamide) (2.8 kg DMF/kg combined mixture). The absorber is operated at 8 bar and is provided with a reboiler and a condensor. The liquid top product consists of 96.8% of propane, 3.0% propylene, 0.2% of propadiene and propyne combined. The bottom product consists of 68.3% DMF, 4.8% propadiene and 14.2% propyne, 8.6% propane and 4.1% propylene.

This mixture is cooled to 35° C. and fed to a first reboiled stripper provided with a condensor, operating at 2.6 bar, where all the propane, propylene, propadiene and part of the propyne are stripped off, resulting in a bottom product consisting of 88.1% DMF and 11.9% methylacetylene with only 10 ppm propadiene. The top product, consisting of 38.2% propane, 18.3% propylene, 21.5% propadiene and 22% propyne is fed to the propadiene isomerization reactor containing an isomerization catalyst where part of the propadiene is converted to propyne, resulting in an effluent containing 4.4% propadiene and 39.1% propyne. This effluent is the recycle stream which is combined with the fresh feed.

The bottom product is fed to a second reboiled stripper equipped with a condensor operating at 1.6 propyne containing only 80 ppm propadiene. The bottom product consists of DMF containing 0.5% propyne, which, after being cooled, is used again in the first absorber. The purpose of the condensors in the strippers is not only to condense the hydrocarbon vapors, but also to remove DMF from the hydrocarbon product.

EXAMPLE 2

Preparation of Catalyst

A 20 % w potassium carbonate on alumina catalyst was prepared as follows: 250 g of 1/16" cylindrical gamma-Al_2O_3 (gamma-alumina) extrudates (pore volume=0.7 ml/g) were activated during 16 hours at 500° C. 50 g of K_2CO_3 (potassium carbonate, Baker analyzed) was dissolved in 150 ml of demineralized water at ambient temperature. 200 g of the activated gamma-Al_2O_3 was contacted with the K_2CO_3 solution and well mixed (incipient wetness method).

After impregnation the catalyst was dried at 125°-140° C. for 16 h. Prior to use the thus obtained 20% w K_2CO_3 on gamma-Al_2O_3 was activated under nitrogen at 575° C. during 24 hours.

Isomerization of Propadiene

Propadiene was isomerized to propyne in a packed bed reactor containing activated K_2CO_3 on gamma-Al_2O_3 catalyst according to the following procedure: A 0.9 cm i.d. stainless steel tube reactor was filled with 2.0 g of K_2CO_3 on gamma-Al_2O_3 catalyst particles. The catalyst was activated according to the temperature treatment described above.

The reactor was fitted in an experimental set-up and a feed mixture of liquefied C_3- and C_4-hydrocarbons was pumped over the catalyst. The feed contained 15% v propadiene, 22% v propyne, 49% v propene, 5% v propane, 3% v 1,3-butadiene and some minor amounts of other C_3- and C_4-hydrocarbons.

At liquid hourly space velocities up to 10 l (feed)/l-(reactor).hr propyne/propadiene isomerization equilibrium was established. The propyne and propadiene concentrations in the reaction product from the above described feed amounted 33.7% v and 3.3% v, when the reaction was carried out at 25° C.

EXAMPLE 3

A 250 ml magnetically stirred autoclave was filled with 0.1 mmol palladium acetate, 1 mmol tri(p-trifluoromethylphenyl)phosphine, 1 mmol methanesulfonic acid, 10 ml methanol and 40 ml anisole.

Air was then evacuated from the autoclave, and then 30 ml propyne was added. Then carbon monoxide was added to a pressure of 20 bar. The autoclave was then sealed and heated to 90° C. Upon completion of the reaction, the contents of the autoclave were analyzed by gas liquid chromatography. The reaction rate was calculated to be 40 g propyne/g Pd/hour.

COMPARATIVE EXAMPLE A

The method of Example 3 was repeated, but using 15 ml propyne and 15 ml allene. The reaction rate was calculated to be 4 g propyne and allene/g Pd/hour.

EXAMPLE 4

A 300 ml magnetically stirred stainless steel autoclave was successively filled with 0.025 mmol palladium(II) acetate, 1 mmol bis(6-methyl-2-pyridyl)-phenylphosphine, 2 mmol paratoluenesulfonic acid, 30 ml N-methylpyrrolidone and 30 ml methanol. Air was evacuated from the autoclave, whereupon 25 ml propyne was added. Subsequently, carbon monoxide was added to a pressure of 60 bar. The autoclave was sealed and heated to a temperature of 80° C. After a reaction time of 1.5 hours at 80° C. a specimen of the contents was analyzed by means of gas liquid chromatography. The mean conversion rate was calculated to be 7500 g propyne/g Pd/hour.

COMPARATIVE EXAMPLE B

The method of Example 4 was repeated, but using 20 ml propyne and 10 ml propadiene instead of 25 ml propyne, and heating to 60° C. No reaction was observed. The autoclave was then heated to 80° C. Again, no

reaction was observed. The autoclave was finally heated to 100° C. Reaction was then observed. The reaction time was 5 hours. The mean conversion rate was calculated to be only 200 g propyne and propadiene/g Pd/hour.

We claim:

1. In a process for the preparation of an alkyl methacrylate by reacting propyne, carbon monoxide and an alkanol in the presence of a palladium carboxylation catalyst, the improvement which comprises:

(a) providing a by-product stream from an ethene cracker, a catalytic cracker or an LPG-dehydrogenation process comprising a C_3 mixture comprising propyne and propadiene;

(b) subjecting said C_3 mixture to extractive distillation or stripping to remove a sufficient amount of the propadiene to form a propyne feed having a molar ratio of propyne to propadiene of at least about 100:1; and

(c) reacting the propyne in said propyne feed with carbon monoxide and an alkanol in the presence of a palladium carboxylation catalyst under conditions effective to produce the alkyl methacrylate.

2. In a process for the preparation of an alkyl methacrylate by reacting propyne, carbon monoxide and an alkanol in the presence of a carboxylation catalyst comprising a Group VIII metal compound, a ligand and an anion of a Bronsted acid, the improvement which comprises:

(a) providing a by-product stream from an ethene cracker, a catalytic cracker or an LPG-dehydrogenation process comprising a C_3 mixture comprising propyne and propadiene;

(b) concentrating said C_3 mixture to provide a concentrated stream having an increased concentration of propyne and propadiene in the C_3 mixture;

(c) subjecting said concentrated stream to extractive distillation or stripping to remove a portion of the propadiene and to produce a propyne feed having a molar ratio of propyne to propadiene of at least 100:1;

(d) contacting any removed propadiene with an isomerization catalyst to provide a recycle stream;

(e) passing said recycle stream to at least one of steps (b), (c), (d) and (f); and

(f) passing said propyne feed to a reaction zone and contacting the propyne therein with carbon monoxide and an alkanol in the presence of a palladium carboxylation catalyst under conditions effective to produce the alkyl methacrylate.

3. The process of claim 1 in which C_3-mixture comprises a by-product stream from an ethene cracker.

4. The process of claim 2 in which said by-product stream is the product of passing at least part of a C_3-stream from a depropanizer to a propane/propene splitter and recovering a bottom effluent.

5. The process of claim 1 in which the mixture of propyne and propadiene in the C_3-mixture has been concentrated by selective scrubbing of the C_3-mixture with a solvent, whereby a solvent stream comprising propyne and propadiene is obtained.

6. The process of claim 5 in which the solvent is selected from the group consisting of dimethylformamide, N-methyl-pyrrolidone, methanol and mixtures thereof.

7. The process of claim 6 in which propadiene is selectively removed by stripping from the solvent stream.

8. The process of claim 7 comprising contacting said removed propadiene with an isomerization catalyst under conditions effective for conversion of propadiene to propyne, and recycling the isomerization product to at least one of step a) and step b).

9. The process of claim 8 in which the isomerization catalyst comprises at least one of an alkali metal on alumina and an alkali metal oxide on alumina.

10. The process of claim 1 in which propadiene is selectively removed by extractive distillation.

11. The process of claim 9 comprising contacting said removed propadiene with an isomerization catalyst under conditions effective for conversation of propadiene to propyne, and recycling the isomerization product to at least one of step a) and step b).

12. The process of claim 1 in which the propyne feed comprises at least 99% (mass) of propyne.

13. The process of claim 1 in which the alkanol is methanol.

14. The process of claim 2 in which the by-product stream comprises the product of introducing at least part of a C_3-hydrocarbon stream from a depropanizer directly into a propane/propene splitter and recovering the bottom effluent.

15. The process of claim 2 wherein the C_3-mixture is concentrated by selective scrubbing with a solvent.

16. The process of claim 2 wherein the C_3-mixture is concentrated by adding the recycled isomerized product thereto.

17. The process of claim 2 wherein the propadiene is removed by contacting the C_3-mixture with an isomerization catalyst at a temperature within the range of from about −30° to about 100° C. and a pressure within the range of about 0.1 to about 100 bar.

18. The process of claim 20 in which the isomerization catalyst comprises at least member selected from the group consisting of an alkali metal on alumina and an alkali metal oxide on alumina.

19. The process of claim 2 wherein the propadiene is selectively removed by extractive distillation.

20. The process of claim 2 wherein the ratio of propyne to propadiene in the propyne feed is at least about 500:1.

21. The process of claim 2 in which the carboxylation catalyst comprises a Group VIII metal compound, a ligand, and an anion of a Broensted acid.

22. The process of claim 21 in which the Group VIII metal compound is palladium.

23. The process of claim 22 in which the ligand is an organic phosphine.

24. The process of claim 23 in which the Broensted acid is an non-halogenic Broensted acid having a $pK_A < 2$.

25. The process of claim 24 in which the propyne feed is contacted at a temperature within the range of about 20° to about 200° C. and a pressure within the range of from about 5 to about 70 bar.

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United States Patent [19]

Drent et al.

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[45] **Date of Patent: Feb. 17, 1998**

[54] **CARBONYLATION CATALYST SYSTEM AND A PROCESS FOR THE CARBONYLATION OF ACETYLENICALLY UNSATURATED COMPOUNDS**

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[52] **U.S. Cl.** **560/207**; 560/97; 560/104; 554/129

[58] **Field of Search** 560/207; 502/167

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[57] **ABSTRACT**

The invention relates to a novel carbonylation catalyst system and a process for the carbonylation of acetylenically unsaturated compounds, whereby a feedstock, comprising an acetylenically unsaturated compound and a relatively minor amount of an 1,2-alkadiene compound, is contacted under carbonylation conditions with carbon monoxide and a hydroxylated co-reactant in the presence of the novel carbonylation catalyst system that is based on:

a) a source of cations of one or more metals of Group VIII of the Periodic Table;

b) a phosphine of the general formulae $PR^1R^2R^3$, $R^1R^2M—R—PR^1R^3$, or $R^2R^3M—R—PR^1R^3$, wherein R^1 represents a substituted or non-substituted 6-membered heteroaryl group having at least one imino nitrogen atom next to the carbon atom that is attached to the phosphorus atom; R^2 represents a halogenated aryl group; R^3 or each of the R^3's represents a substituted or non-substituted (hetero)hydrocarbyl group, M is an element of Group Va, preferably a nitrogen or phosphorus atom, R represents a bridging (substituted) hydrocarbyl group having 1 to 4 carbon atoms in the bridge; and

c) a source of protons.

11 Claims, No Drawings

CARBONYLATION CATALYST SYSTEM AND A PROCESS FOR THE CARBONYLATION OF ACETYLENICALLY UNSATURATED COMPOUNDS

FIELD OF THE INVENTION

The invention relates to a novel carbonylation catalyst system and a process for the carbonylation of acetylenically unsaturated compounds, whereby a feedstock, comprising an acetylenically unsaturated compound and a relatively minor amount of an 1,2-alkadiene compound, is contacted under carbonylation conditions with carbon monoxide and a hydroxylated co-reactant in the presence of the novel carbonylation catalyst system.

BACKGROUND TO THE INVENTION

Generally, the feedstocks available for the carbonylation of acetylenically unsaturated compounds additionally contain 1,2-alkadiene compounds (so-called allenes). Typically, the presence of these 1,2 alkadiene compounds, even in relatively small amounts (say up to 0.4%), unfavorably affects the activity of the catalyst system. Therefore, special measures to purify the feedstocks need to be taken, before they can be used for the carbonylation process.

In International application WO 95/05357, a carbonylation catalyst system is disclosed, that comprises a certain (mono or bidentate) (di)phosphine bearing for instance 6-halo-2-pyridyl groups on the phosphorus atom as ligand to the transition metal, that easily outperforms the already fine catalyst system disclosed in EP-A-0,441,446 and even performs satisfactorily in the presence of 7.0% v of 1,2-alkadiene impurities. However, it remains desirable to be able to use alternative catalyst systems of at least similar competence. Moreover, as the carbonylation reaction produces heat, a carbonylation catalyst system is looked for that on the one hand can feed on feedstocks comprising an acetylenically unsaturated compound and a relatively minor amount of an 1,2-alkadienes, and on the other hand is stable at temperatures in the range of 70 to 100° C.

SUMMARY OF THE INVENTION

The invention may be defined as relating to a novel carbonylation catalyst system and to a process for the carbonylation of acetylenically unsaturated compounds, whereby a feedstock comprising an acetylenically unsaturated compound and a relatively minor amount of an 1,2-alkadiene compound is contacted under carbonylation conditions with carbon monoxide and a hydroxylated co-reactant, in the presence of the novel catalyst system. The novel catalyst system is based on:

a) a source of cations of one or more metals of Group VIII of the Periodic Table;

b) a phosphine of the general formulae $PR^1R^2R^3$, $R^1R^2M—R—PR^3R^3$, or $R^2R^3M—R—PR^1R^3$, wherein R^1 represents a substituted or non-substituted 6-membered heteroaryl group having at least one imino nitrogen atom next to the carbon atom that is attached to the phosphorus atom; R^2 represents a halogenated aryl group; R^3 or each of the R^3's represents a substituted or non-substituted (hetero) hydrocarbyl group. M is an element of Group Va, preferably a nitrogen or phosphorus atom, R represents a bridging (substituted) hydrocarbyl group having 1 to 4 carbon atoms in the bridge; and

c) a source of protons.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The metals as regards component a) of the catalyst system include iron, cobalt, ruthenium, rhodium, iridium, and osmium, but in particular nickel, palladium and platinum. Preferably, the catalyst system is based on a source of palladium cations.

The source of cations of metals of Group VIII may be the metallic element or a metal compound, such as a metal salt or a complex of the metal with a phosphine, with carbon monoxide or with acetylacetonate. It is advantageously a metal compound, in particular a metal salt. Examples of suitable metal salts are salts of sulfuric acid, nitric acid, sulfonic acids, phosphonic acids, perhalic acids and carboxylic acids, such as alkane carboxylic acids with 1 to 12 carbon atoms, for example acetic acid and propionic acid, or halogenated carboxylic acids, for example trichloroacetic acid and trifluoroacetic acid. Palladium acetate has proved to be a particularly suitable source of metal cations.

As regards component b) of the catalyst system, R^1 may for instance be a 2-pyridyl-, or the radical of any of the diazines, triazines or tetrazines. Moreover, the 6-membered ring system may be part of a larger, fused ring system (e.g., (iso)quinolinyl-, a radical of any of the benzodiazines or benzotriazines). Preferably, the phosphine is substituted with a 2-pyridyl group. Suitable substituents on the 6-membered heteroaryl group include alkyl groups, for example methyl and ethyl groups, amino and (di)alkylamino groups and halogen atoms.

R^2 is a phenyl group or a larger aryl group having at least one or more halogen atoms substituted thereon. Suitably, the halogen atoms are chlorine or bromine atoms. More suitably, R^2 is a phenyl group having one or more chlorine atoms substituted thereon. The location of the or each halogen atom is not very important, i.e., excellent results have been achieved with meta-chlorine substituents.

R^3 or each of the R^3's preferably represents a substituted or unsubstituted pyridyl, alkyl or aryl group, and—more preferably—is identical to either R^1 or R^2. Examples of suitable R^3 groups are 2-pyridyl, phenyl, tolyl, xylyl, and cyclohexyl groups and alkyl groups having from 3 to 7 carbon atoms. Phosphines wherein both R^2 and R^3 represent a halogenated phenyl group are preferred.

Preferably, the phosphine is a monophosphine of the general formula $PR^1R^2R^3$.

As regards component c) of the catalyst system, the source of protons may be provided by a protonic acid or even traces water. Indeed, the protonic acid may be generated in situ, for instance, upon addition of a Lewis acid to the hydroxylated co-reactant, or by carbonylation of the acetylenically unsaturated compound with water into the corresponding acid. Lewis acids that are suitably used include halogenated arylborates, BF_3, $AlCl_3$, SnF_2, $Sn(CF_3SO_3)_2$, $SnCl_2$, $GeCl_2$ and PF_5.

Preferably, the protonic acid has a substantially non-coordinating anion, i.e. an anion which does not, or only to a very minor extent, coordinate with the metal of Group VIII. Preferred acids in this respect include: sulfuric acid; sulfonic acids; halogenated carboxylic acids such as trifluoroacetic acid; perhalic acids such as perchloric acid, and acidic ion exchange resins such as a sulphonated ion exchange resin. Optionally substituted alkylsulfonic acids, such as methanesulfonic acid, trifluoromethanesulfonic acid and tert-butylsulfonic acid are examples of very preferred protonic acids.

The number of moles of phosphine and of moles of protonic acid per mole (of atoms) of the metal of Group VIII may vary considerably. Recommended phosphine amounts are in the range of 10 to 100 moles of phosphine per mole of the metal of Group VIII and in particular in the range of

20 to 80. The amount of protonic acid is preferably selected such that per mole of the metal of Group VIII, 2 to 500 moles of protonic acid are present.

The catalyst system of the invention may be homogeneous or heterogeneous. Preferably, it is homogeneous. The amount in which the catalyst is applied in the process of the invention is suitably selected such that per mole of acetylenically unsaturated compound to be converted, from 10^{-8} to 10^{-1} mole of the Group VIII metal is present, preferably from 10^{-7} to 10^{-2} on the same basis.

Suitable acetylenically unsaturated compounds, to be used as starting material in the process of the invention, include optionally substituted alkynes with 2 to 20 carbon atoms per molecule. Examples are acetylene, propyne, 1-butyne, 2-butyne, 1-hexyne, phenyl acetylene and benzylethyne. Preferably, unsubstituted alkynes with 3 to 10 carbon atoms are used.

In view of the industrial outlets for the carbonylated products, propyne is a preferred starting material.

As has been stated above, a major advantage of the catalyst systems of the invention consists in their tolerance towards 1,2-alkadiene compounds in the acetylenic feedstocks. Accordingly, commercially available feedstocks may be used that containing small amounts of 1,2-alkadiene compounds, such as propadiene, in addition to the acetylenically unsaturated compounds. In general, a 1,2-alkadiene content of at most 0.1 mole per mole (e.g., 10%), based on acetylenically unsaturated compound, can be tolerated. It is recommended to use feedstocks in which the amount of 1,2alkadiene compounds is lower, suitably in the range of 0.002 to 0.05 moles per mole of acetylenically unsaturated compound.

The hydroxylated co-reactant may be any hydroxyl-containing compound such as a monohydric, dihydric or polyhydric alkanol, a phenol, or water.

Monohydric alkanols are preferred, in particular those having from 1 to 4 carbon atoms. Among these, methanol is most preferred.

The co-reactant is suitably used in excess, thereby avoiding the need of a separate diluent or solvent. However, a liquid diluent may be applied, if so desired. Preferably, non-alkaline diluents are used, such as ketones, e.g. methylisobutylketone, or ethers, e.g. dipropylether or 2,5,8-trioxanonane.

Owing to the high activity of the catalysts, the process of the invention proceeds readily at moderate reaction conditions. Suitable reaction temperatures are, for instance, in the range of 20 to 150° C., preferably in the range of 30 to 100° C.

The reaction pressure is usually selected in the range of 1 to 100 bar. Preferably, the pressure is in the range of 5 to 70 bar.

The invention is illustrated with the following, non-limiting examples.

EXAMPLES

All experiments were carried out in a 250 ml "Hastelloy C" (trade mark) magnetically stirred autoclave. The autoclave was charged with 0.025 mmoles (5.6 mg) of palladium (II) acetate, the selected phosphine and protonic acid in the amounts indicated hereafter, and 50 ml of methanol.

Air was evacuated from the autoclave, whereupon 30 ml of a feedstock containing propyne and propadiene was added.

Subsequently, carbon monoxide was supplied up to a pressure of 60 bar. The autoclave was sealed and heated to the desired reaction temperature.

As soon as the falling pressure remained constant (marking the completion of the reaction), the contents of the autoclave were cooled and a sample was withdrawn and analyzed by gas liquid chromatography.

Example I

a) An experiment was carried out in the manner as outlined above, whereby as phosphine 2 mmol (0.53 g) of bisphenyl(2-pyridyl)phosphine and as protonic acid 2 mmol (130 µl) of methanesulfonic acid was used. The feed was propyne, containing 1.9% of propadiene. The reaction temperature was 90 C.

The reaction time (completion) was 1 hour. Analysis showed that methyl methacrylate (MMA) had been formed with a selectivity of 98.7% at a propyne conversion of about 100%. The average reaction rate was calculated to be 25,800 moles of product per mole of palladium and per hour (mol/mol.hr).

b) The experiment described under a) was repeated at 80° C. with the difference that as phosphine 2 mmol (0.66 g) of bis(3-chlorophenyl)(2-pyridyl)phosphine was used.

The reaction time was 1 hour. Analysis showed that MMA had been formed with a selectivity of about 98.5% at a propyne conversion of about 100%. The average reaction rate was calculated to be 50,000 mol/mol.hr.

Example II

a) An experiment was carried out in the manner as outlined above, whereby as phosphine 1 mmol (0.26 g) of bisphenyl(2-pyridyl)phosphine and as protonic acid 2 mmol (130 µl) of methanesulfonic acid were used. The feed was propyne, containing 2.3% of propadiene. The reaction temperature was 90° C.

The reaction time (completion) was 5 hours. Analysis showed that MMA had been formed with a selectivity of 98.6% at a propyne conversion of about 84%. The average reaction rate was calculated to be 5,000 mol/mol.hr.

b) The experiment described under a) was repeated at 80° C. with the difference that as phosphine 1 mmol (0.33 g) of bis(3-chlorophenyl)(2-pyridyl)phosphine was used.

The reaction time was 10 hours. Analysis showed that MMA had been formed with a selectivity of 98.5% at a propyne conversion of about 86%. The average reaction rate was calculated to be 7,200 mol/mol.hr.

c) The experiment described under b) was repeated with the difference that as phosphine 2 mmol (0.66 g) of bis(3-chlorophenyl)(2-pyridyl)phosphine was used.

The reaction time was 2 hours. Analysis showed that MMA had been formed with a selectivity of 98.5% at a propyne conversion of about 100%. The average reaction rate was calculated to be 48,800 mol/mol.hr.

Example III

An experiment was carried out in the manner as outlined above, whereby as phosphine 4 mmol (1.42 g) of bis(3-chlorophenyl)(6-chloro-2-pyridyl)phosphine and as protonic acid 5 mmol (325 µl) of methanesulfonic acid were used. The feed was propyne, containing 3.6% of propadiene. The reaction temperature was 80° C.

The reaction time was 1 hour. Analysis showed that MMA had been formed with a selectivity of 99.6% at a propyne conversion of about 100%. The average reaction rate was calculated to be 12,000 mol/mol.hr.

Example IV

An experiment was carried out in the manner as outlined above, whereby as phosphine 2 mmol (0.71 g) of bis(3-

chlorophenyl)(6-chloro-2-pyridyl)phosphine and as protonic acid 2 mmol (180 μl) of trifluoromethanesulfonic acid were used. The feed was propyne, containing 5.1% of propadiene. The reaction temperature was 85° C.

The reaction time was 5 hours. Analysis showed that MMA had been formed with a selectivity of 99.6% at a propyne conversion of about 86%. The average reaction rate was calculated to be 12,500 mol/mol.hr.

These examples demonstrate that the catalyst systems of the present invention (alike the comparative catalyst system based on a non-substituted phosphine) are sufficiently stable at elevated temperatures.

In comparative Examples I(a) and II(a), with a non-substituted phosphine as catalyst component, the reaction rates for convening feedstocks containing propadiene are low even at high temperatures due to the (inhibitive) presence of the propadiene. In Examples I(b), II(b), and II(c), however, the use of the halogenated phosphines of the present invention results in considerably higher reaction rates. Indeed, in Examples III and IV, a feedstock comprising 3.6%, respectively 5.1% of propadiene was convened at high yield and selectivity.

We claim:

1. A carbonylation catalyst comprising:

a) a source of cations of one or more metals of Group VIII of the Periodic Table;

b) a phosphine of the general formula selected from the group consisting of $R^1R^2M—R—PR^3R^3$, and $R^2R^3M—R—PR^1R^3$, wherein R^1 represents a substituted or non-substituted 6-membered heteroaryl group having at least one imino nitrogen atom next to the carbon atom that is attached to the phosphorus atom; R^2 represents a halogenated aryl group; R^3 or each of the R^3's represents a substituted or non-substituted (hetero) hydrocarbyl group, M is an element of Group Va, R represents a bridging hydrocarbyl group having 1 to 4 carbon atoms in the bridge; and

c) a source of protons.

2. The catalyst of claim 1, wherein the metal of component a) is selected from the group consisting of nickel, platinum and palladium.

3. The catalyst of claim 1, wherein the metal of component a) is palladium.

4. The catalyst of claim 1, wherein component b) comprises a phosphine wherein R^1 represents a 2-pyridyl group.

5. The catalyst of claim 1 wherein component b) comprises a phosphine wherein R^2 represents a phenyl group having one or more chlorine atoms substituted thereon.

6. A catalyst of claim 1 wherein component b) comprises a phosphine wherein R^3 or each of the R^3's represents a substituted or non-substituted pyridyl, alkyl or aryl group.

7. A catalyst of claim 5 wherein component b) comprises a phosphine wherein both R^2 and R^3 represent a halogenated phenyl group.

8. A process for the carbonylation of acetylenically unsaturated compounds, the process comprising the steps of:

providing a feedstock, the feedstock comprising an acetylenically unsaturated compound and a relatively minor amount of an 1,2-alkadiene compound;

contacting the feedstock, under conditions effective to carbonylate the feedstock, with carbon monoxide and a hydroxylated co-reactant, in the presence of a catalyst system comprising

a) a source of cations of one or more metals of Group VIII of the Periodic Table,

b) a phosphine selected from the group consisting of $R^1R^2M—R—PR^3R^3$ and $R^2R^3M—R—PR^1R^3$, wherein R^1 represents a substituted or non-substituted 6-membered heteroaryl group having at least one imino nitrogen atom next to the carbon atom that is attached to the phosphorus atom; R^2 represents a halogenated aryl group; R^3 or each of the R^3's represents a substituted or non-substituted (hetero)hydrocarbyl group, M is an element of Group Va, R represents a bridging hydrocarbyl group having 1 to 4 carbon atoms in the bridge, and

c) a source of protons; and recovering the carbonylated feedstock.

9. The process of claim 8, wherein the amount of 1,2-alkadiene compound in the feedstock is less than 0.1 mole per mole of acetylenically unsaturated compound.

10. The process of claim 9, wherein the molar amount of 1,2-alkadiene compound in the feedstock per mole of acetylenically unsaturated compound is in the range of 0.002 to 0.05.

11. The process of claim 8 wherein the recovered carbonylated feedstock is methyl methacrylate and the feedstock comprises propyne and 1,2-propadiene.

* * * * *

Optimization of Extractive Distillation Column

Number of Trays	Condenser Heat Duty [BTU/hr]	Reboiler Heat Duty [BTU/hr]	Cost of Proposed Column (over 15 years, in MM)	Cost of Steam	Cost of CW	Cost of Trays
50	6587364	8601136	3.8447	$3,418,585	$156,617	$83,293
70	5780861	7797484	3.5992	$3,099,167	$137,442	$116,610
83	5572030	7593605	3.5728	$3,018,134	$132,477	$138,266
85	5533508	7555705	3.5659	$3,003,071	$131,561	$141,597
87	5497982	7520907	3.5604	$2,989,240	$130,716	$144,929
88	5497241	7520790	3.5648	$2,989,193	$130,699	$146,595
89	**5465320**	**7489003**	**3.5560**	**$2,976,559**	**$129,940**	**$148,261**
90	5464601	7488919	3.5605	$2,976,526	$129,923	$149,927
100	5356090	7385252	3.5619	$2,935,323	$127,343	$166,585
102	5355899	7386263	3.5714	$2,935,724	$127,338	$169,917
107	5312663	7345695	3.5767	$2,919,600	$126,310	$178,246
108	5312595	7346285	3.5814	$2,919,835	$126,309	$179,912
110	5293310	7328033	3.5827	$2,912,581	$125,850	$183,244
120	5242244	7282738	3.6082	$2,894,578	$124,636	$199,902
150	5119141	7177735	3.6965	$2,852,843	$121,709	$249,878

ASSUMPTIONS:

$4 / 1000lb steam

Constant Diam = 1.37m

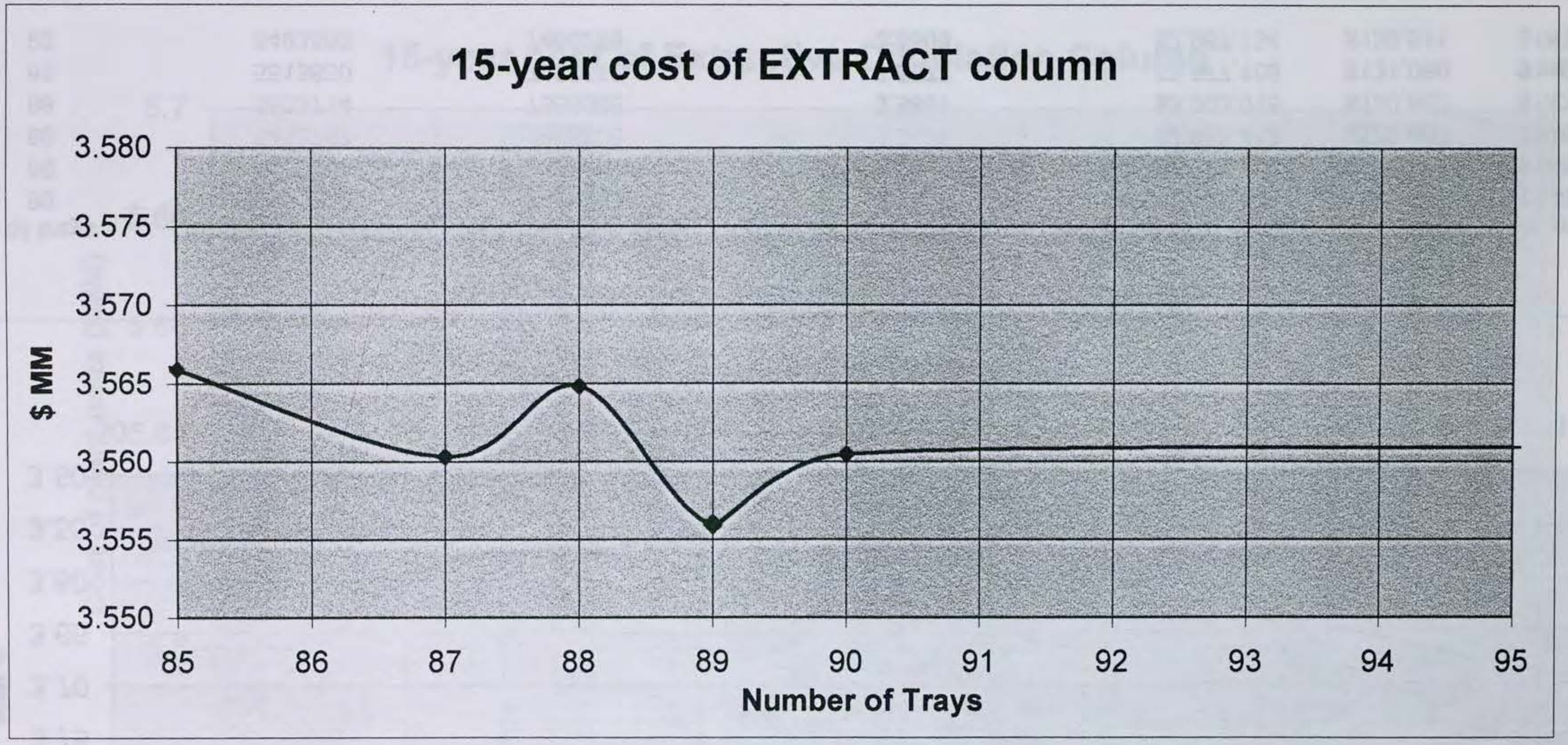
No P effect on cost

Nr/Ns = 1.82

% col. above feed 64.6%

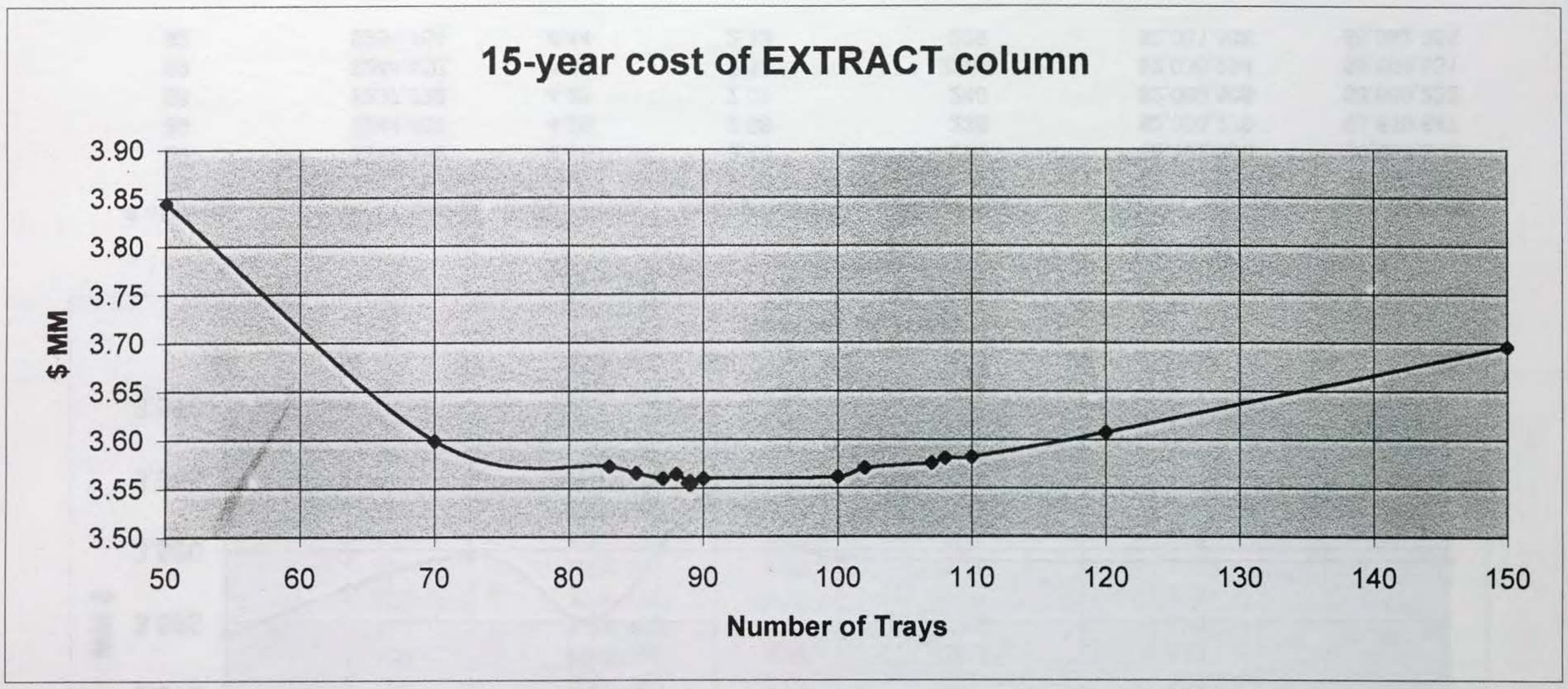
Optimization of Extractive Distillation Column

Number of Trays	Cost of Vessel	Reflux Ratio	Boilup Ratio	Amount of MeOH [lbmol/hr]
50	$154,347	5.56	2.44	230
70	$201,317	4.72	2.21	230
83	$230,963	4.50	2.15	230
85	$235,472	4.46	2.14	230
87	$239,968	4.42	2.13	230
88	$242,211	4.42	2.13	230
89	**$244,452**	**4.39**	**2.13**	**230**
90	$246,689	4.39	2.13	230
100	$268,899	4.28	2.10	230
102	$273,308	4.28	2.10	230
107	$284,284	4.23	2.09	230
108	$286,471	4.23	2.09	230
110	$290,839	4.21	2.08	230
120	$312,533	4.16	2.07	230
150	$376,350	4.03	2.04	230



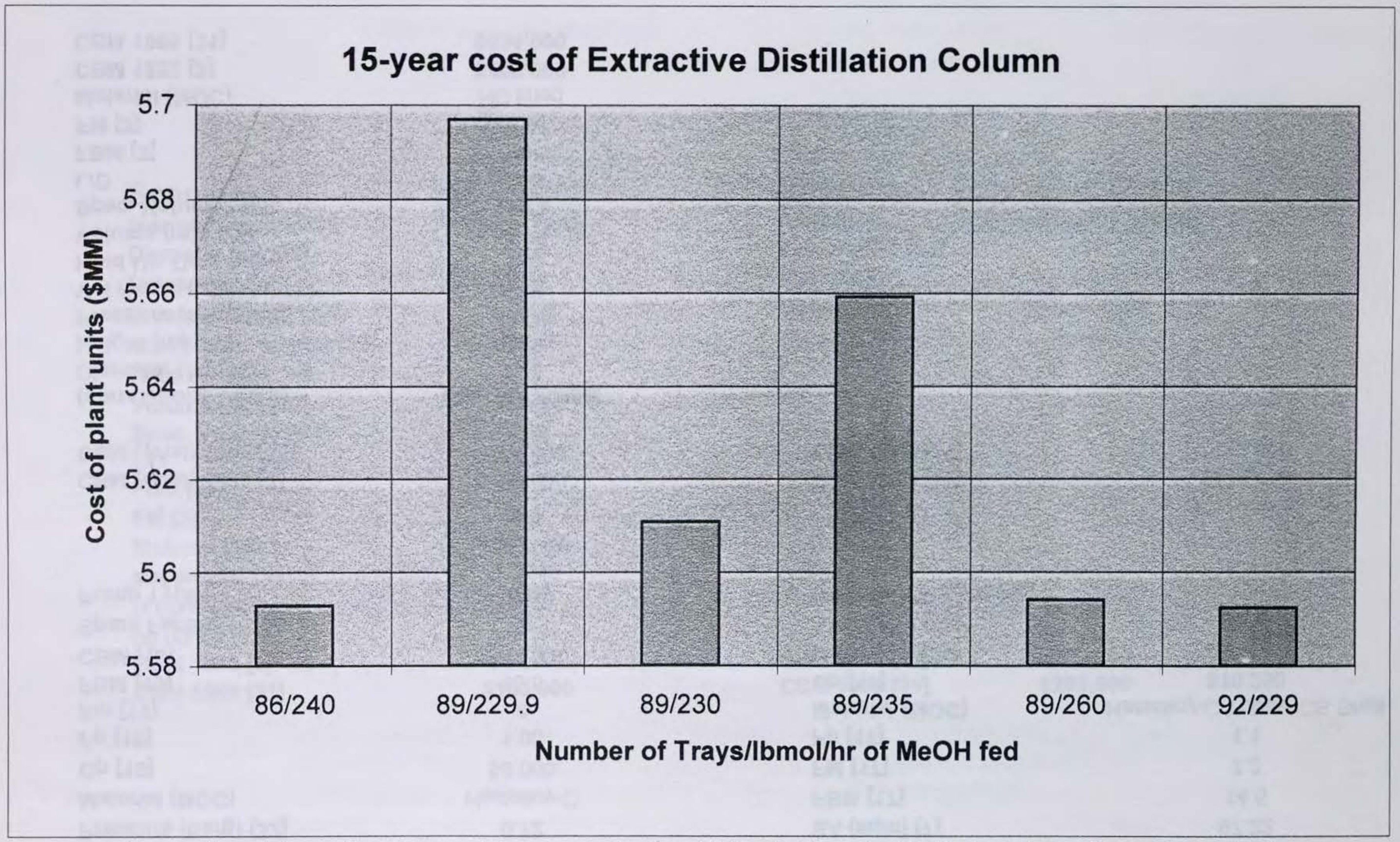
Small-scale view of the minimization of cost curve for the Extractive Distillation column

# of trays	Cost of Vessel	Reflux Ratio	Boilup Ratio	Moles MeOH	Cost of Plant Units	Cost of Plant
89	$244,452	4.39	2.13	230	$2,036,826	$5,592,814
89	$244,452	4.39	2.13	260	$2,192,306	$5,696,836
89	$244,452	4.29	2.08	235	$2,063,279	$5,610,847
86	$237,722	4.26	2.07	240	$2,089,508	$5,659,222
89	$244,452	4.39	2.13	229.9	$2,036,294	$5,594,031
92	$251,154	4.44	2.13	229	$2,031,508	$5,592,355



Large-scale view of the minimization of cost curve for the Extractive Distillation column

# of trays	Condenser Heat Duty	Reboiler Heat Duty	Cost of Proposed Column ($MM)	Cost of Steam	Cost of CW	Cost of Trays
89	5465320	7489003	**3.5560**	$2,976,559	$129,940	$148,261
89	5170247	7377186	**3.5045**	$2,932,117	$122,924	$148,261
89	5453787	7468508	**3.5476**	$2,968,413	$129,665	$148,261
86	5503714	7555565	**3.5697**	$3,003,015	$130,852	$143,263
89	5513630	7490512	**3.5577**	$2,977,159	$131,088	$148,261
92	5493563	7465289	**3.5608**	$2,967,134	$130,611	$153,258



A comparison of the number of trays and the amount of methanol fed to the Extractive Distillation column with the plant unit price

Scenario 1 — One flash

(correlations Ulrich)	Catalyst Reactor Feed Pump
Shaft Power (kW) [32,18]	6.83
Pressure (psi) [32]	25
Pressure (barg) [32]	0.72
Material (MOC)	Hastelloy-C
Cp [19]	$9,000
Fp [19]	1.00
Fm [19]	9
FBM [19]	15.5
CBM [19]	$140,000
Spare Factor	2
Pump Type	Rotary
CBM (total) 1982 [3]	**$280,000**
CBM (total) 1999 [31]	**$356,000**

(correlations Ulrich)	Reactor Vessel
Diameter (m) [32]	1.96
Height (m) [29]	4.89
Pressure (barg) [32]	58.98
Vol Flow (cuft/min) [32]	8.67
Hold Up Time (min)	60
Volume (m3) [28]	14.73
Spec. Volume (m3)	14.73
L/D	2.50
FBM [3]	19
FM [3]	5.5
Material (MOC)	HC lined
CBM 1982 [3]	**$499,000**
CBM 1999 [31]	**$634,000**

Reactor and Accessory Costs

(correlations Ulrich)	Reactor Heat Exchanger
Pressure (barg) [32]	59
SA (sqft) [7]	1046.46
SA (sqm) [7]	97.22
FBM [17]	14.5
FM [17]	7.2
Fp [17]	1.1
Material (MOC)	Hastelloy-C Tubes/ CS Shell
Cp [17]	$10,250
Q (Btu/hr) [32]	12,533,992
ΔTLM (°F) [32]	79.9
U (Btu/hr °F sqft) [32]	150
CBM 1982 [17]	**$149,000**
CBM 1999 [31]	**$190,000**

Scenario 1 — One flash

(correlations Ulrich)	Flash Tank
Diameter (m) [32]	1.18
Height (m) [29]	3.54
Pressure (barg) [32]	0.2058
Vol Flow (cuft/min) [32]	4786.53
Hold Up Time (min)	10
Volume (m3) [22]	1355.96
Spec. Volume (m3)	3.89
L/D	2.5
FBM [3]	13.5
FM [3]	5.5
Material (MOC)	HC lined
superficial velocity (m/s) [23]	1.1446
ρl (lb/ft^3) [32]	54.56
ρg (lb/ft^3) [32]	0.17
CBM 1982 [3]	**$81,000**
CBM 1999 [31]	**$103,000**

Vessel and Accessory Costs

(Ulrich)	Catalyst AZEO Blower
Power (kW) [32]	161
FBM [19]	2.2
Material	Carbon Steel
Type	Rotary

CBM 1982 [19]	**$230,000**
CBM 1999 [31]	**$293,000**

Scenario 1	One flash	Utility Costs
(correlations SSL)	**Remove Cat**	**Reactor Exchanger**
Q [Btu/hr] [32]	4,595,867	12,533,992
CW temp in (°F) [32]		90
CW temp out (°F) [32]		120
Stream temp in (°F) [32]		194
Stream temp out (°F) [32]		176
ΔT[LM] (°F) [32]		79.85
Cp CW (lb/hr) [32]		1
Δ H [vap] BTU/lb [7a]	853	
mass flow utility (lb/hr) [32]	5,388	156,970
1000 gal CW / lb MMA [33]		0.0015
cost / 1000 gal ($)		0.05
cost / 1000 lb LP steam($)	6	
cost / yr ($)	256,032	7,464
1000 lb steam / lb MMA	0.000426721	
cost / 15 yrs	**$3,841,000**	**$112,000**
Total Utility Cost	**$3,953,000**	

Scenario 2 — Two flashes

(correlations Ulrich)	Catalyst Reactor Feed Pump
Shaft Power (kW) [32]	1.31
Pressure (psi) [32]	25
Pressure (barg) [32]	0.72
Material (MOC)	Hastelloy-C
Cp [19]	$4,500
Fp [19]	1.00
Fm [19]	9
FBM [19]	15.5
CBM [19]	$70,000
Spare Factor	2
Pump Type	Rotary
CBM (total) 1982	**$140,000**
CBM (total) 1999 [31]	**$178,000**

(correlations Ulrich)	Reactor Vessel
Diameter (m) [32]	1.91
Height (m) [29]	4.78
Pressure (barg) [32]	58.98
Vol Flow (cuft/min) [32]	8.09
Hold Up Time (min)	60
Volume (m3) [28]	13.75
Spec. Volume (m3)	13.75
L/D	2.50
FBM [3]	19
FM [3]	5.5
Material (MOC)	HC lined
CBM 1982 [3]	**$475,000**
CBM 1999 [31]	**$604,000**

Reactor and Accessory Costs

(correlations Ulrich)	Reactor Heat Exchanger
Pressure (barg) [32]	59
SA (sqft) [7]	1045.79
SA (sqm) [7]	97.16
FBM [17]	14.5
FM [17]	7.2
Fp [17]	1.1
Material (MOC)	Hastelloy-C Tubes/ CS Shell
Cp [17]	$10,250
Q (Btu/hr) [32]	12,525,909
ΔTLM (°F) [32]	79.9
U (Btu/hr °F sqft) [32]	150
CBM 1982 [3,17]	**$149,000**
CBM 1999 [31]	**$190,000**

Scenario 2 — Two flashes

(correlations Ulrich)	Flash Tank 1	Flash Tank 2
Diameter (m) [32]	1.20	1.18
Height (m) [29]	3.60	3.54
Pressure (barg) [32]	0.2058	0.01
Vol Flow (cuft/min) [32]	2734.18	2392.68
Hold Up Time (min)	10	10
Volume (m3) [22]	774.56	677.81
Spec. Volume (m3)	4.06	3.89
L/D	2.5	2.5
FBM [3]	13.5	13.5
FM [3]	5.5	5.5
Material (MOC)	HC lined	HC lined
superficial velocity (m/s)[23]	1.270082006	1.144761573
ρl (lb/ft^3) [32]	58.7500	54.5600
ρg (lb/ft^3) [32]	0.1488	0.17
CBM 1982 [3]	**$83,000**	**$81,000**
CBM 1999 [31]	**$106,000**	**$103,000**
Total CBM 1999	**$209,000**	

Vessel and Accessory Costs

(Ulrich)	Cat. Azeo. Blower	Interflash Blower
Power (kW) [32]	161.31	32.62
FBM [19]	2.2	22
Material	Carbon Steel	Hastelloy C
Type	Rotary	Rotary
CBM 1982 [19]]	**$230,000**	**$504,000**
CBM 1999 [31]	**$293,000**	**$640,000**
Total CBM 1999	**$933,000**	

Scenario 2	Two flashes		Utility Costs
(correlations SSL)	**Flash 1**	**Flash 2**	**Reactor Exchanger**
Q [Btu/hr] [32]	4,600,204	83818.586	12,525,909
CW temp in (°F) [32]			90
CW temp out (°F) [32]			120
Stream temp in (°F) [32]			194
Stream temp out (°F) [32]			176
ΔT[LM] (°F) [32]			79.85
Cp CW (lb/hr) [32]			1
Δ H [vap] BTU/lb [7a]	853	853	
mass flow utility (lb/hr) [32]	5,393	98	156,868
1000 gal CW / lb MMA [33]			0.0015
cost / 1000 gal ($)			0.05
cost / 1000 lb steam($)	6	6	
cost / yr ($)	256,274	4,669	7,459
1000 lb steam / lb MMA	0.000427123	7.78245E-06	
cost / 15 yrs	**$3,845,000**	**$71,000**	**$112,000**
Total Utility Cost	**$4,028,000**		

Scenario 3 — Column without condenser

(correlations Ulrich)	Catalyst Reactor Feed Pump
Shaft Power (kW) [32,18]	0.131
Pressure (psi) [32]	25
Pressure (barg) [32]	0.72
Material (MOC)	Hastelloy-C
Cp [19]	$2,000
Fp [19]	1.00
Fm [19]	9
FBM [19]	15.5
CBM [19]	$31,000
Spare Factor	2
Pump Type	Rotary

Reactor and Accessory Costs

(correlations Ulrich)	Reactor Heat Exchanger
Pressure (barg) [32]	59
SA (sqft) [7]	1044.96
SA (sqm) [7]	97.08
FBM [17]	14.5
FM [17]	7.2
Fp [17]	1.1
Material (MOC)	Hastelloy-C Tubes/ CS Shell
Cp [17]	$10,250
Q (Btu/hr) [32]	12,516,053
ΔTLM (°F) [32]	79.9
U (Btu/hr °F sqft) [32]	150

CBM (total) 1982 [19]	**$62,000**	**CBM 1982 [17]**	**$149,000**
CBM (total) 1999 [31]	**$79,000**	**CBM 1999 [31]**	**$190,000**

(correlations Ulrich)	Reactor Vessel
Diameter (m) [32]	1.90
Height (m) [29]	4.76
Pressure (barg) [32]	58.98
Vol Flow (cuft/min) [32]	7.97
Hold Up Time (min)	60
Volume (m3) [28]	13.54
Spec. Volume (m3)	13.54
L/D	2.50
FBM [3]	19
FM [3]	5.5
Material (MOC)	HC lined
CBM 1982 [3]	**$470,000**
CBM 1999 [31]	**$597,000**

Scenario 3 — Column without condenser

(correlations Ulrich)	Column
Tray Spacing (in) [32]	20
Diameter (m) [32]	1.044
Height per column (m) [29]	3.86
No. Trays [32]	2
Actual No. Trays [4]	4
Pressure (barg) [32]	0.01
FBM [3]	12
fq [4]	2.5
FM [3]	5.5
Tray Efficiency (%) [32]	0.7
Material (MOC)	HC lined
Fp [3]	1.2
CBM (sieve) [4]	$34,000
CBM (column) [3]	$75,000
CBM (Column, Trays & Reboiler) 1982	$202,000
CBM (Column, Trays & Reboiler) 1993 [31]	$257,000

(correlations Ulrich)	Reboiler
Pressure (barg) [32]	1.519875116
SA (sqft) [7]	454.85
SA (sqm) [7]	42.26
FBM [17]	9
FM [17]	4.9
Fp [17]	1
Material (MOC)	HC lined
Cp [17]	$10,250
Q (Btu/hr) [32]	4,548,475
heat flux (Btu/hr sqft) [7]	10000
CBM 1982 [17]	$93,000

Vessel and Accessory Costs

(Ulrich)	Catalyst AZEO Blower
Power (kW) [32]	194
FBM [19]	2.2
Material	Carbon Steel
Type	Rotary
CBM 1982 [19]	$274,000
CBM 1999 [31]	$348,000

Scenario 3 (correlations SSL)	Column without condenser Reboiler	Reactor Heat Exchanger	Utility Costs
Q [Btu/hr] [32]	4,548,475	12,516,053	
CW temp in (°F) [32]		90	
CW temp out (°F) [32]		120	
Stream temp in (°F) [32]		194	
Stream temp out (°F) [32]		176	
ΔT[LM] (°F) [32]		79.85	
Cp CW (lb/hr) [32]		1	
Δ H [vap] BTU/lb [7a]	853		
mass flow utility (lb/hr) [32]	5,332	156,745	
1000 gal CW / lb MMA [33]		0.0015	
cost / 1000 gal ($)		0.05	
cost / 1000 lb HP steam($)	8		
cost / yr ($)	337,856	7,453	
1000 lb steam / lb MMA	0.00042232		
cost / 15 yrs	**$5,068,000**	**$112,000**	
Total Utility Cost	**$5,180,000**		

Scenario 3 Column without condenser Tray Optimization

# of Trays	Act. # of Trays	Q Reboiler [MM BTU/hr]	(D in m)	(H in m)	(P in Psi)	(P in barg)	fq
2	4	4.5485	1.044023821	3.860846948	14.70	0.01	2.5
5	8	4.5497	1.04396515	5.892871657	14.70	0.01	1.83
8	13	4.5500	1.043921902	8.432902544	14.70	0.01	1.35

# of Trays	Act. # of Trays	Cost of HP Steam	Cost of Trays	Cost of Vessel	Cost of Proposed Column (over 15 years)	Cost in $MM
2	4	$5,067,843	$33,909	$74,027	**$5,175,779**	5.18
5	8	$5,069,251	$49,641	$106,937	**$5,225,829**	5.23
8	13	$5,069,598	$59,507	$146,057	**$5,275,162**	5.28

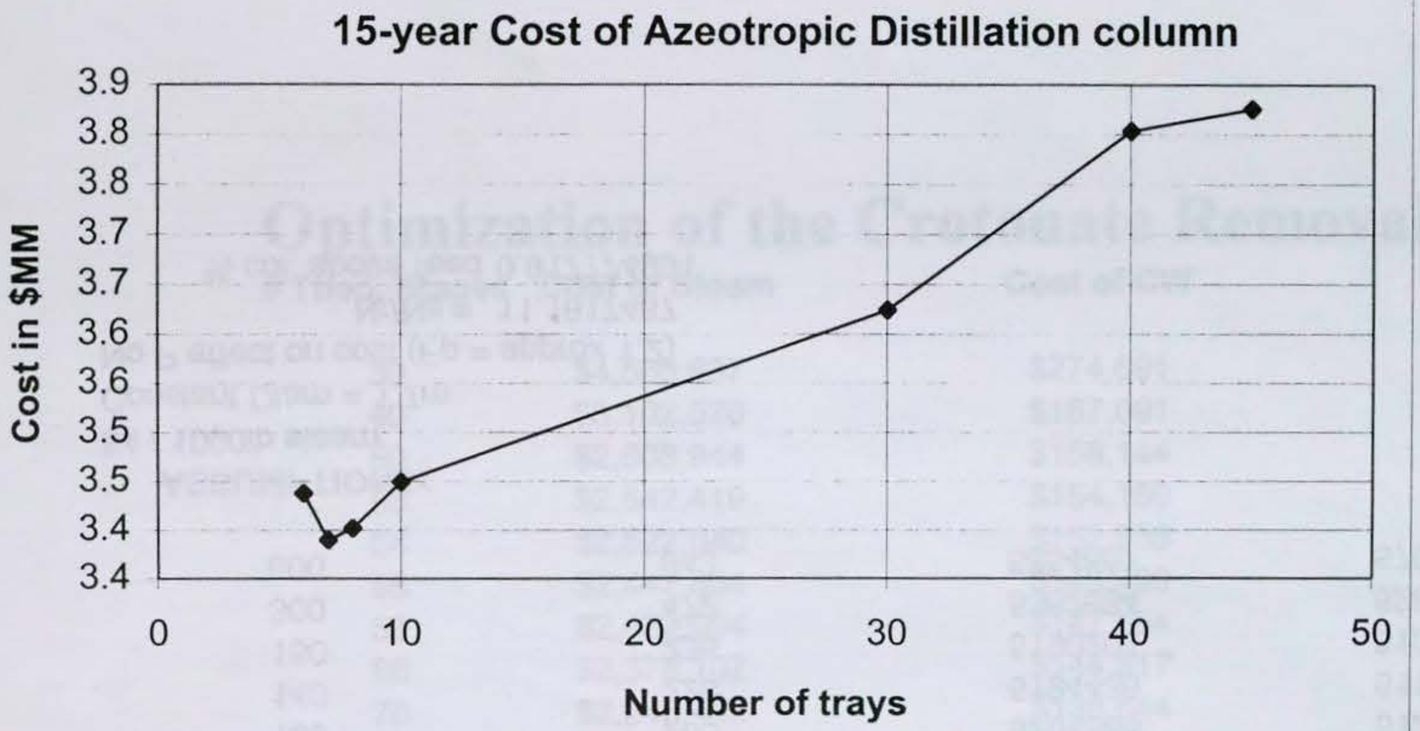
Optimization of Azeotropic Distillation Column

ASSUMPTIONS:

$4 / 1000lb LP steam
Constant Column Diameter = 1.7m
Nr/Ns = 0.222178335
% col. above feed 18.18
Reflux Ratio = 3

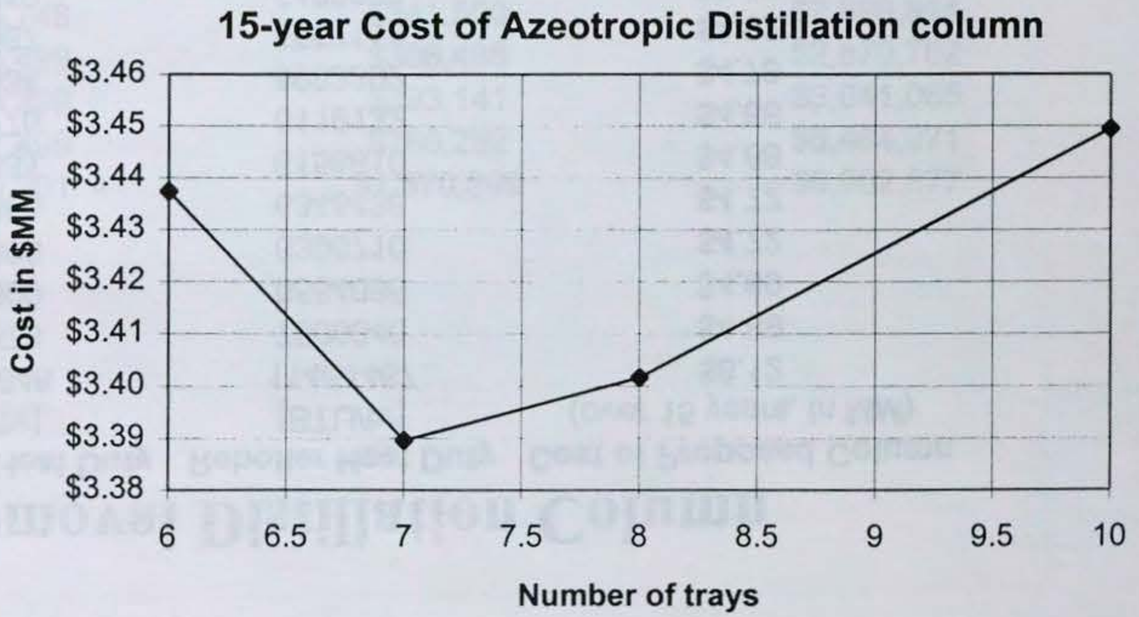
Number of Stages	Cost of Proposed Column (over 15 years, in MM)	Cost of Steam	Cost of CW	Cost of Trays	Cost of Vessel
6	$3.44	$2,798,587	$161,720	$9,995	$326,511
7	**$3.39**	**$2,747,265**	**$158,461**	**$11,661**	**$350,059**
8	$3.40	$2,738,385	$157,843	$13,327	$373,372
10	$3.45	$2,737,956	$157,686	$16,659	$419,367
20	$3.43	$2,564,291	$146,223	$33,317	$639,789
30	$3.62	$2,542,959	$144,276	$49,976	$849,168
40	$3.80	$2,518,840	$142,177	$66,634	$1,051,016
45	$3.83	$2,462,299	$138,349	$74,963	$1,149,731

Number of Stages	Condenser Heat Duty [BTU/hr]	Reboiler Heat Duty [BTU/hr]	Add'l cost due to reduced stages	lbmol/hr recycle
6	6802021	7041225	$140,463	109.25
7	**6664956**	**6912100**	**$122,054**	**106.89**
8	6638955	6889758	$118,604	106.45
10	6632336	6888680	$117,741	106.34
20	6150204	6451740	$49,494	97.79
30	6068327	6398069	$37,278	96.29
40	5980013	6337386	$24,246	94.70
45	5819041	6195127	$0	91.77



Small-scale view of minimization of cost curve for Azeotropic Distillation column by varying the number of trays.

Large-scale view of minimization of cost curve for Azeotropic Distillation column by varying the number of trays.



Optimization of the Crotonate Removal Distillation Column

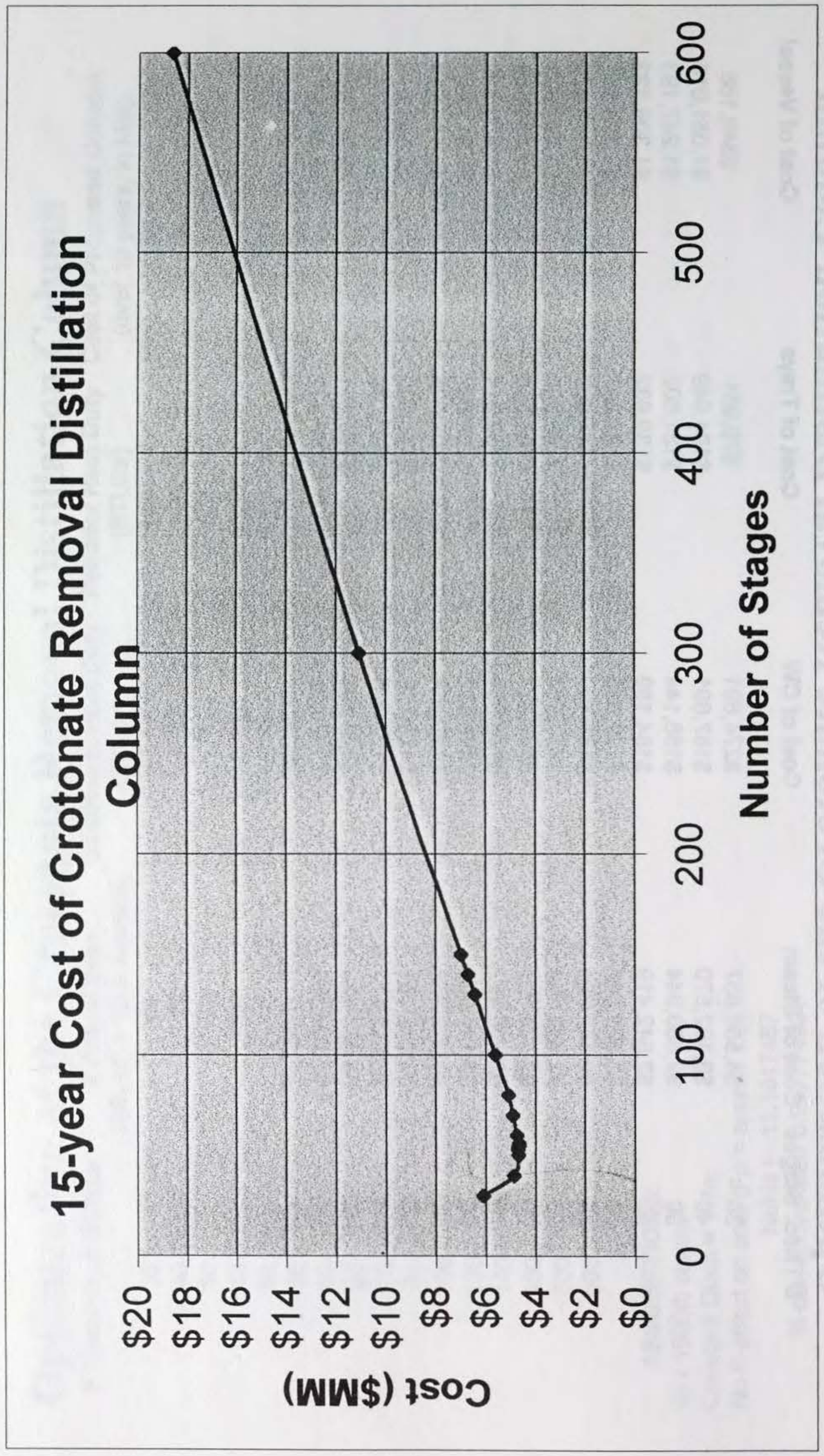
# Theoretical Stages	# Actual trays	Condenser Heat Duty	Reboiler Heat Duty	Cost of Proposed Column
	70% eff + 10% oversize	[BTU/hr]	[BTU/hr]	(over 15 years, in MM)
30	48	11553646	11464467	$6.12
40	63	7894373	7806046	$4.89
50	79	6651600	6564085	$4.69
53	84	6483990	6396710	$4.72
54	85	6432663	6345436	$4.72
55	87	6245931	6158810	$4.68
56	88	6206175	6119132	$4.68
60	95	6070034	5983302	$4.76
70	110	5743087	5657116	$4.92
80	126	5487310	5402062	$5.12
100	158	5300395	5216555	$5.64
130	205	5204885	5123018	$6.46
140	220	5194436	5113195	$6.72
150	236	5190201	5109570	$7.00
300	472	5362684	5289939	$11.07
600	943	5854867	5793854	$18.64

ASSUMPTIONS:

$4 / 1000lb steam
Constant Diam = 1.7m
No P effect on cost (Fp = approx 1.2)
Nr/Ns = 11.1617487
% col. above feed 0.917774991

Optimization of the Crotonate Removal Distillation Column

# Theo. Stages	Cost of Steam	Cost of CW	Cost of Trays	Cost of Vessel
30	$4,556,637	$274,691	$79,961	$849,168
40	$3,102,570	$187,691	$104,949	$1,051,016
50	$2,608,944	$158,144	$131,602	$1,247,193
53	$2,542,419	$154,159	$139,932	$1,305,123
54	$2,522,040	$152,938	$141,597	$1,324,347
55	$2,447,864	$148,499	$144,929	$1,343,529
56	$2,432,094	$147,554	$146,595	$1,362,671
60	$2,378,107	$144,317	$158,256	$1,438,843
70	$2,248,462	$136,544	$183,244	$1,626,740
80	$2,147,089	$130,462	$209,897	$1,811,440
100	$2,073,358	$126,018	$263,205	$2,172,833
130	$2,036,181	$123,748	$341,500	$2,698,914
140	$2,032,277	$123,499	$366,488	$2,870,762
150	$2,030,836	$123,399	$393,141	$3,041,085
300	$2,102,525	$127,499	$786,282	$5,464,971
600	$2,302,810	$139,201	$1,570,899	$9,902,877



Large-scale view of the cost minimization curve used to optimize the crotonate removal distillation column

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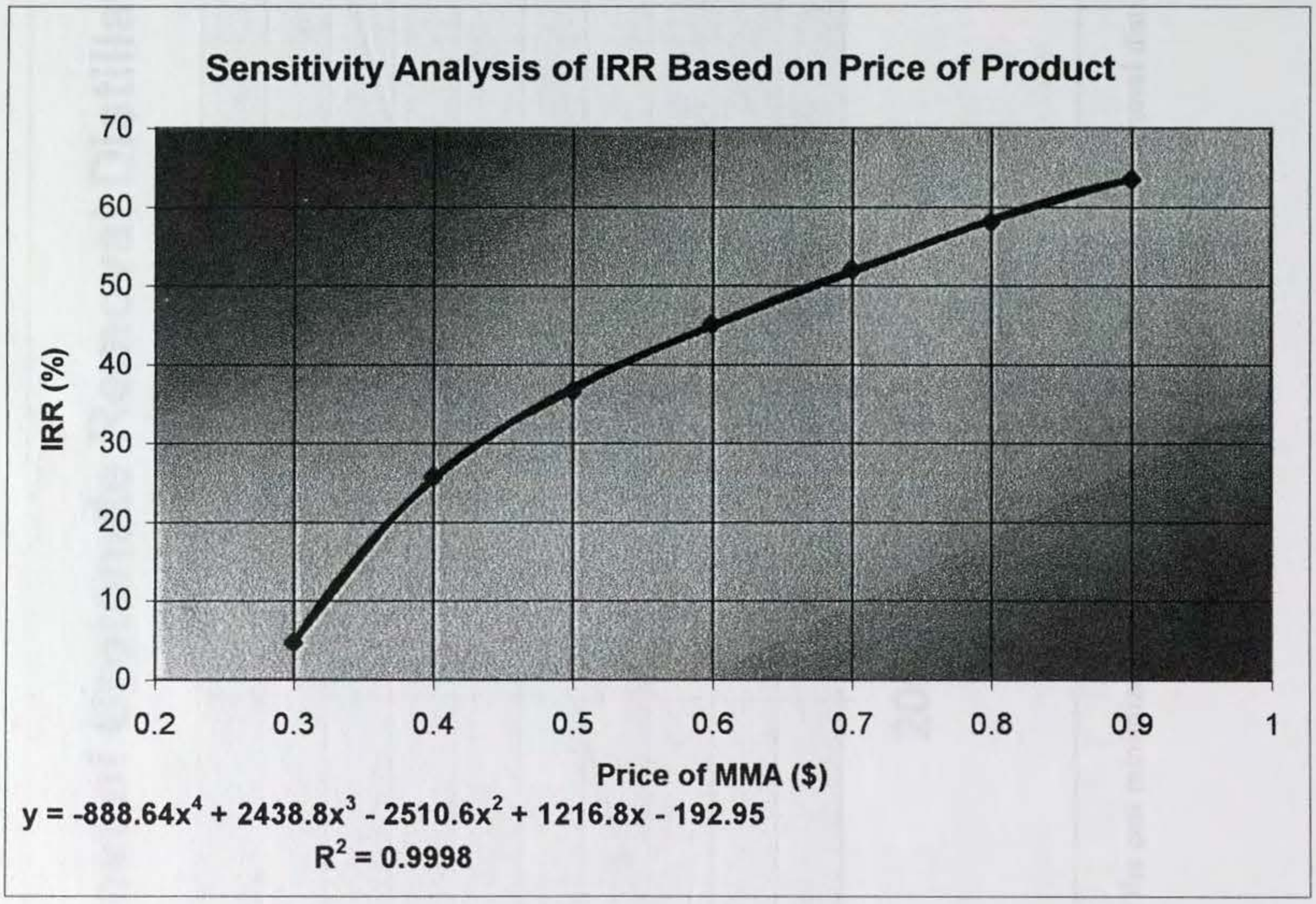
I. Economic Sensitivity Analysis

IRR for different prices were calculated by the Economics Excel Sheet Programs [38]

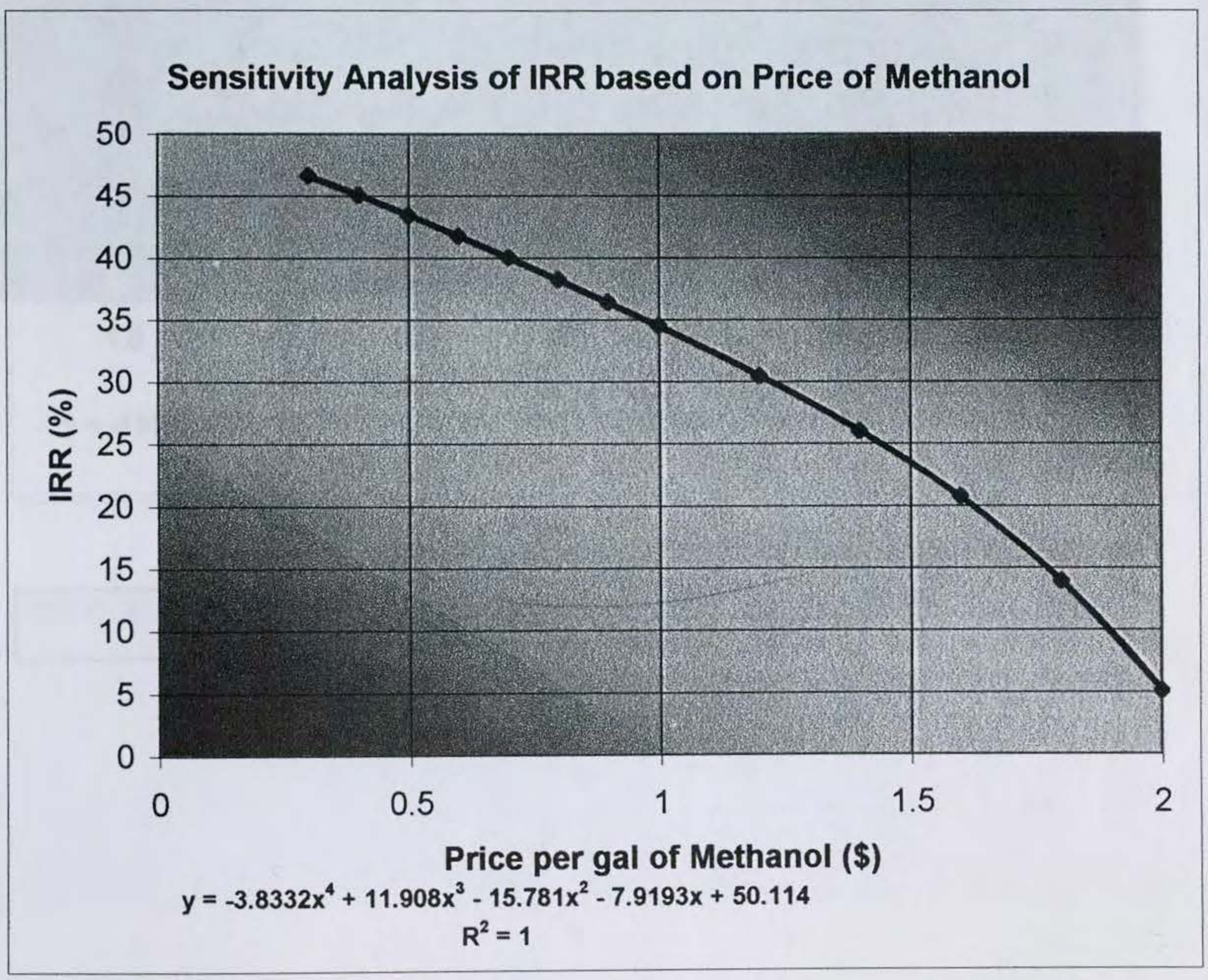
Price per lb MMA ($)	IRR (%)
0.3	4.7
0.4	25.76
0.5	36.62
0.6	45.06
0.7	52.06
0.8	58.12
0.9	63.52



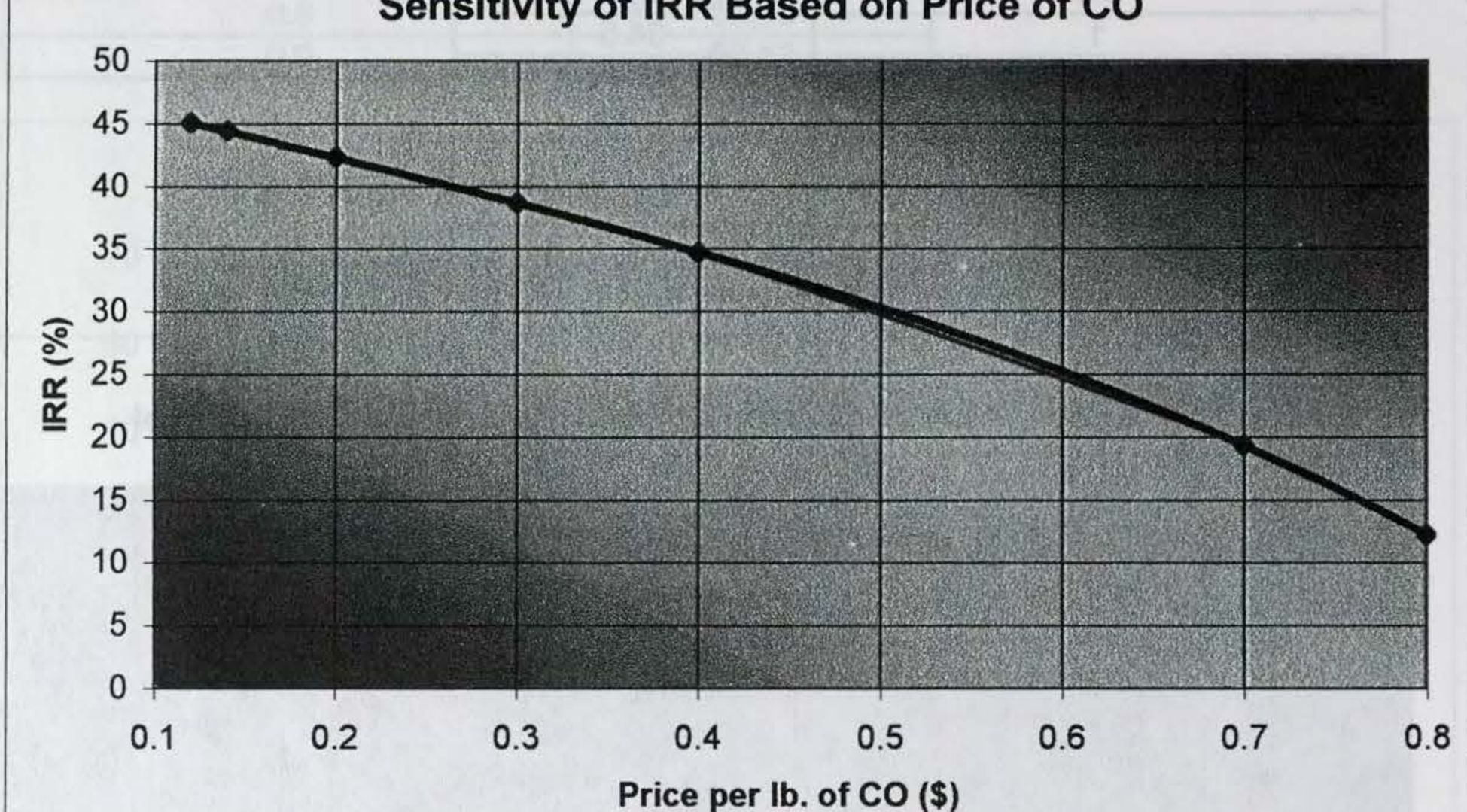
IRR (%)	Price at 20% IRR ($)
20.07	0.37

IRR (%)	Price @ 20% IRR ($)
20.00	1.62

Price per gal Methanol ($)	IRR (%)
0.3	46.64
0.4	45.06
0.5	43.42
0.6	41.74
0.7	40.02
0.8	38.24
0.9	36.4
1	34.5
1.2	30.46
1.4	26.02
1.6	20.74
1.8	13.94
2	5.08

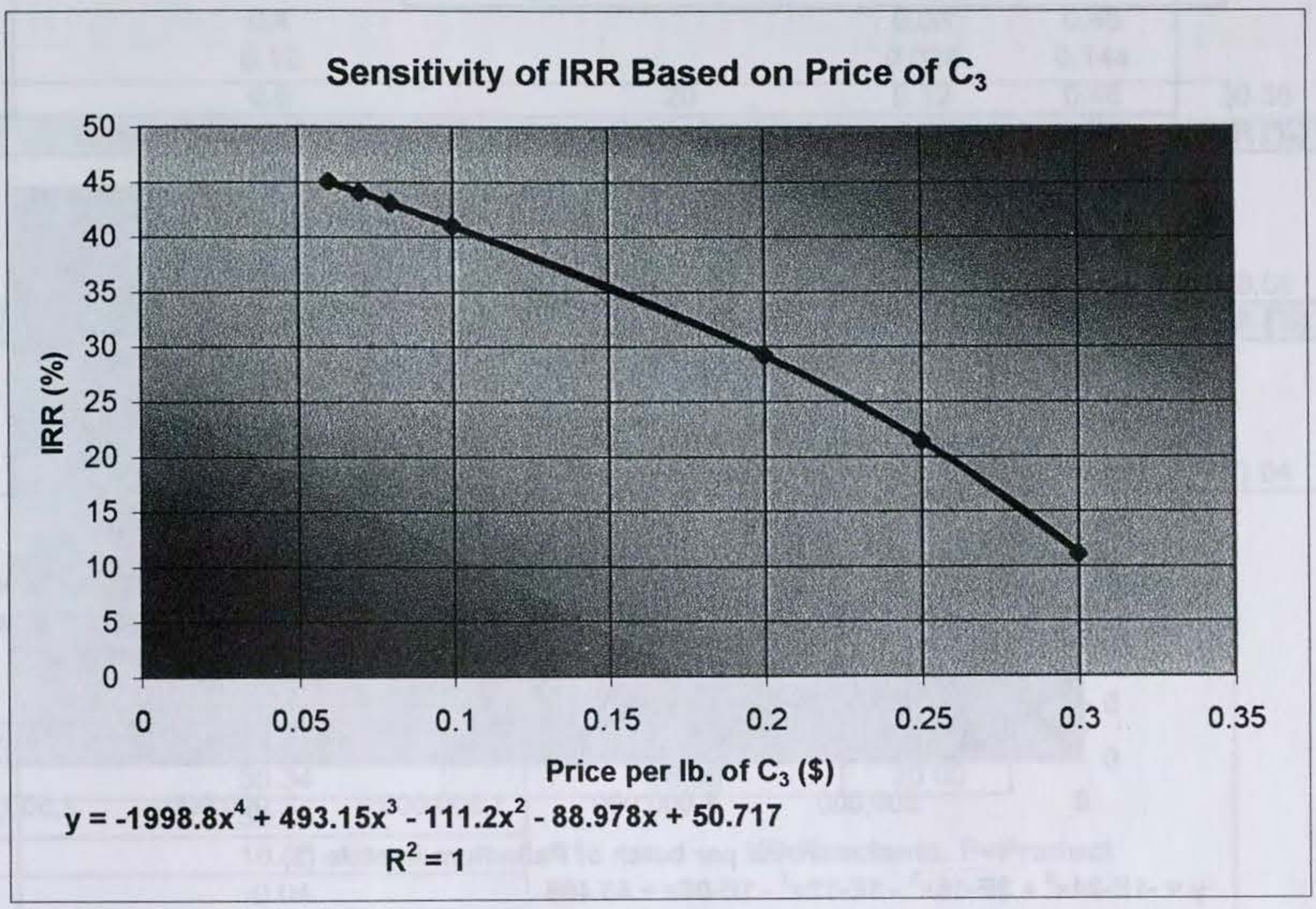


Price per lb. CO ($)	IRR (%)
0.12	45.06
0.14	44.38
0.2	42.3
0.3	38.64
0.4	34.72
0.7	19.34
0.8	12.24



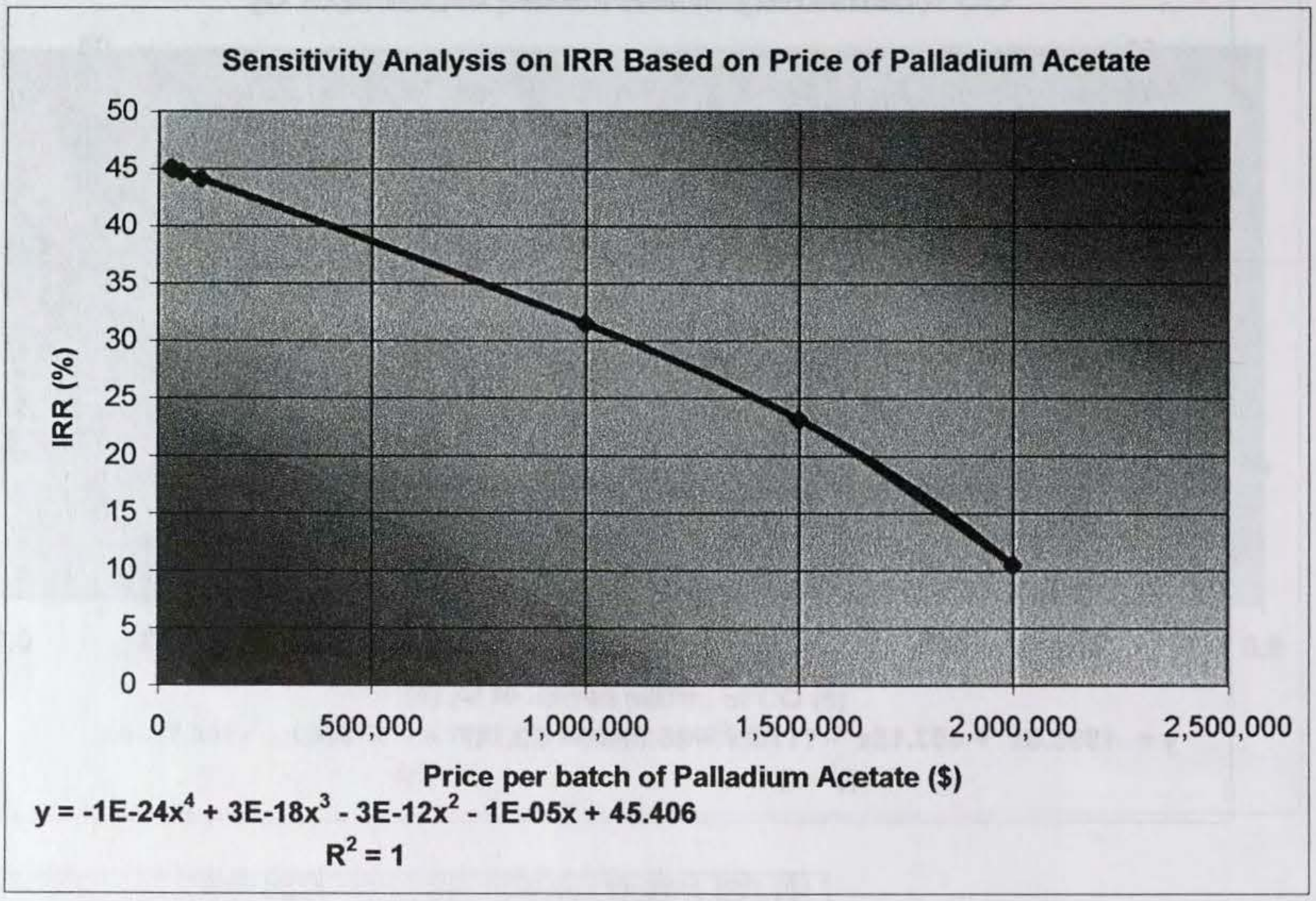
IRR (%)	Price @ 20% IRR ($)
20.00	0.69

Price per lb C_3 ($)	IRR (%)
0.06	45.06
0.07	44.06
0.08	43.06
0.1	41
0.2	29.22
0.25	21.42
0.3	11.14



IRR (%)	Price @ 20% IRR ($)
20.00	0.26

Price per batch Palladium Ac ($)	IRR (%)
30000	45.04
31000	45.02
35000	44.96
55000	44.72
100000	44.14
1000000	31.56
1500000	23.16
2000000	10.52



IRR (%)	Price @ 20% IRR ($)
20.00	2,075,189.31

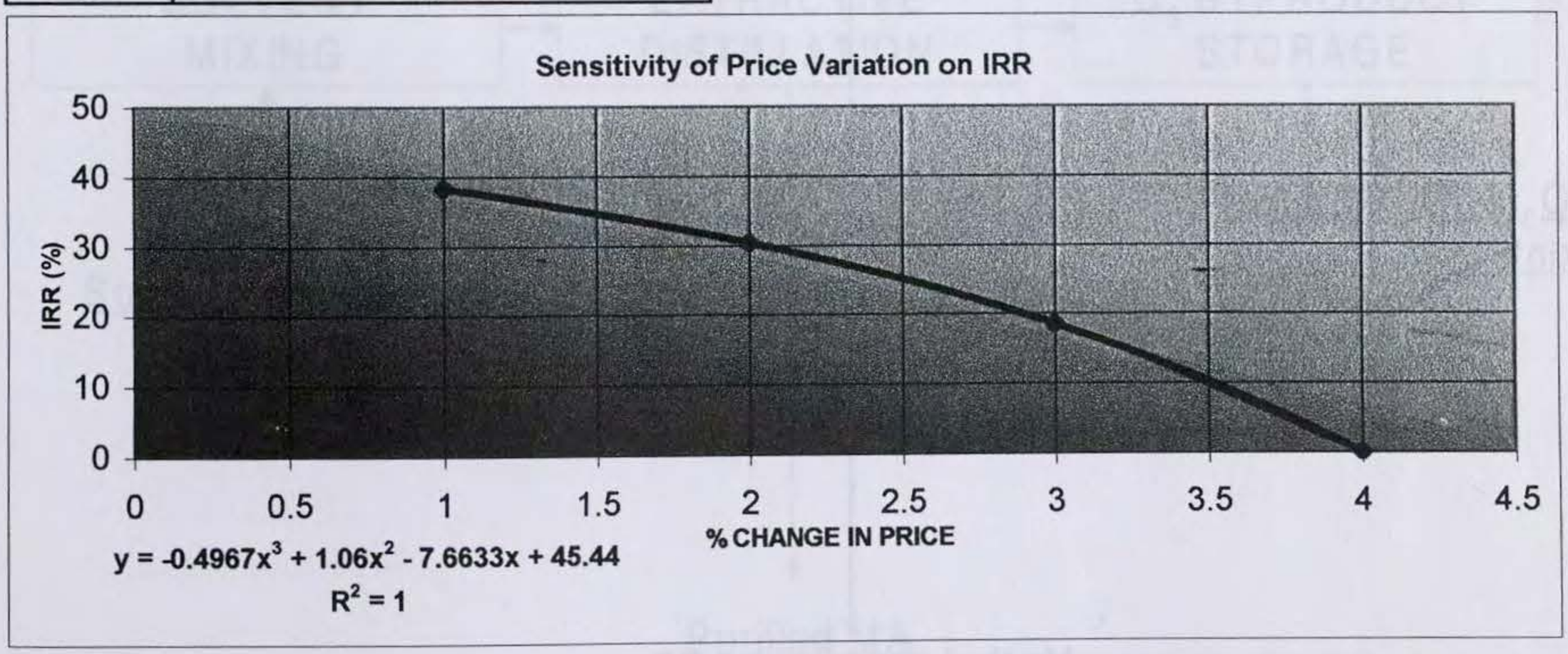
SENSITIVITY OF PRICE CHANGE ON IRR

	Original Cost of Material ($)	Reactant ΔPRICE%	%of Price	New Price	IRR (%)
C3	0.06	10	0.006	0.066	
Methanol	0.4		0.04	0.44	
CO	0.12		0.012	0.132	
M M A	0.6	10	0.06	0.54	38.34
	Original Cost of Material ($)	**Reactant ΔPRICE%**	**%of Price**	**New Price**	**IRR (%)**
C3	0.06	20	0.012	0.072	
Methanol	0.4		0.08	0.48	
CO	0.12		0.024	0.144	
M M A	0.6	20	0.12	0.48	30.38
	Original Cost of Material ($)	**Reactant ΔPRICE%**	**%of Price**	**New Price**	**IRR (%)**
C3	0.06	30	0.018	0.078	
Methanol	0.4		0.12	0.52	
CO	0.12		0.036	0.156	
M M A	0.6	30	0.18	0.42	18.58
	Original Cost of Material ($)	**Reactant ΔPRICE%**	**%of Price**	**New Price**	**IRR (%)**
C3	0.06	40	0.024	0.084	
Methanol	0.4		0.16	0.56	
CO	0.12		0.048	0.168	
M M A	0.6	40	0.24	0.36	-0.04

The above table investigates the effect on IRR if all reactant prices increase by the shown percentage and if product price is decreased by the shown percentage. Even with a 20% increase in reactant price and 20% decrease in product price the IRR is 30.38%.

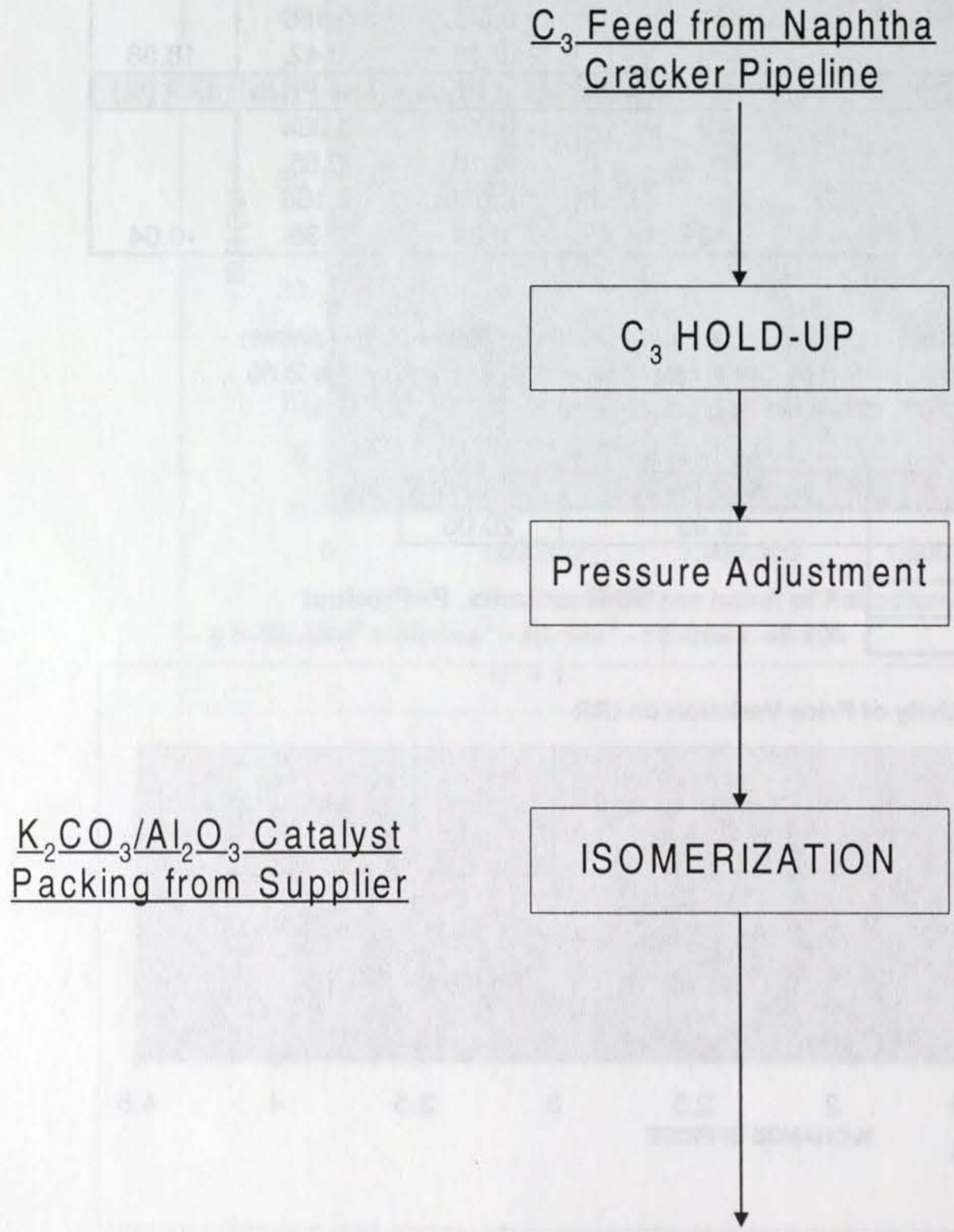
Δ% +R,−P	IRR (%)	Δ% @ 20% IRR	IRR (%)
10*	38.34	28.96	20.00
20*	30.38		
30*	18.58		
40*	-0.04		

***R=Reactants, P=Product**

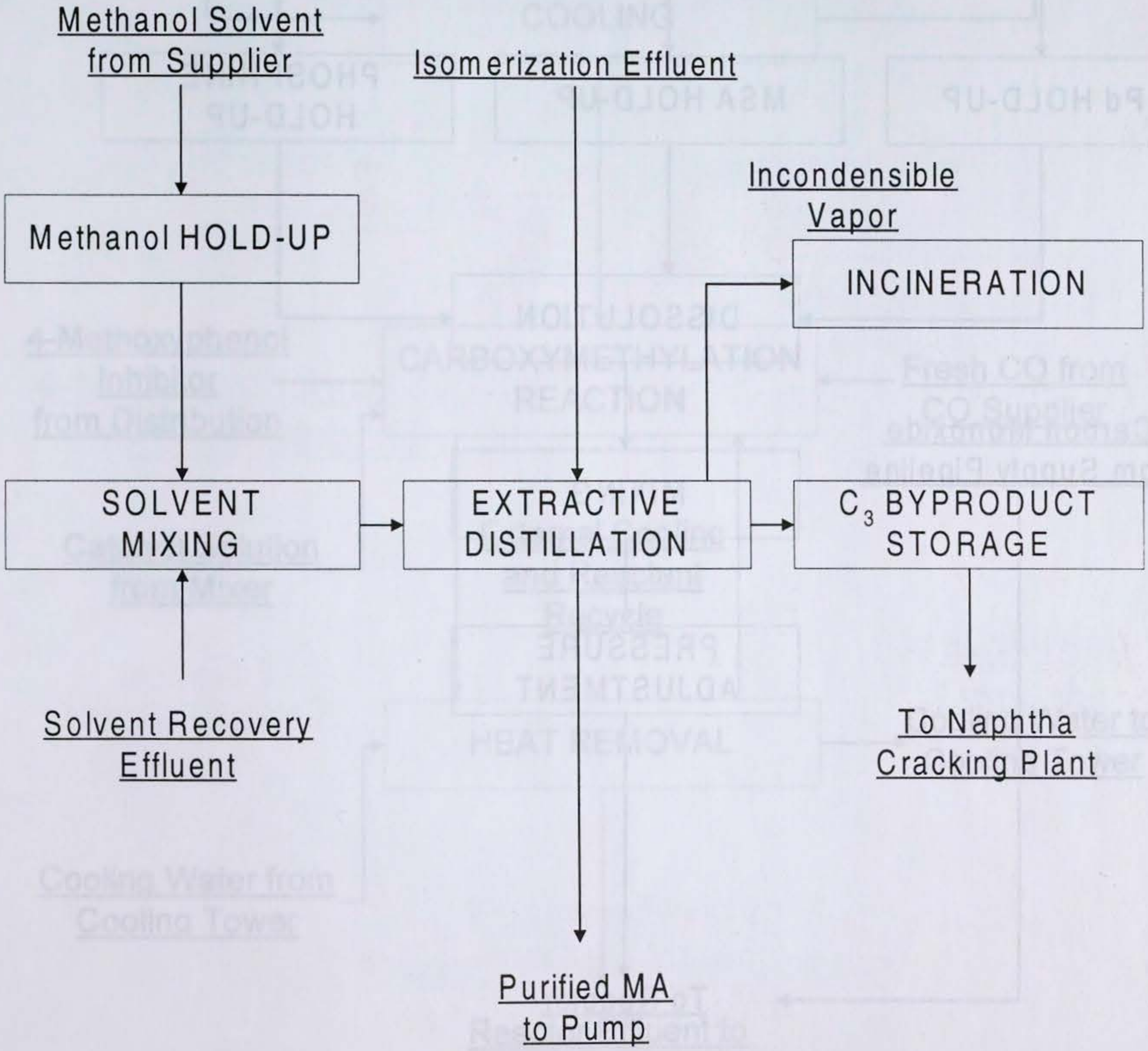


J. Process Block Diagrams

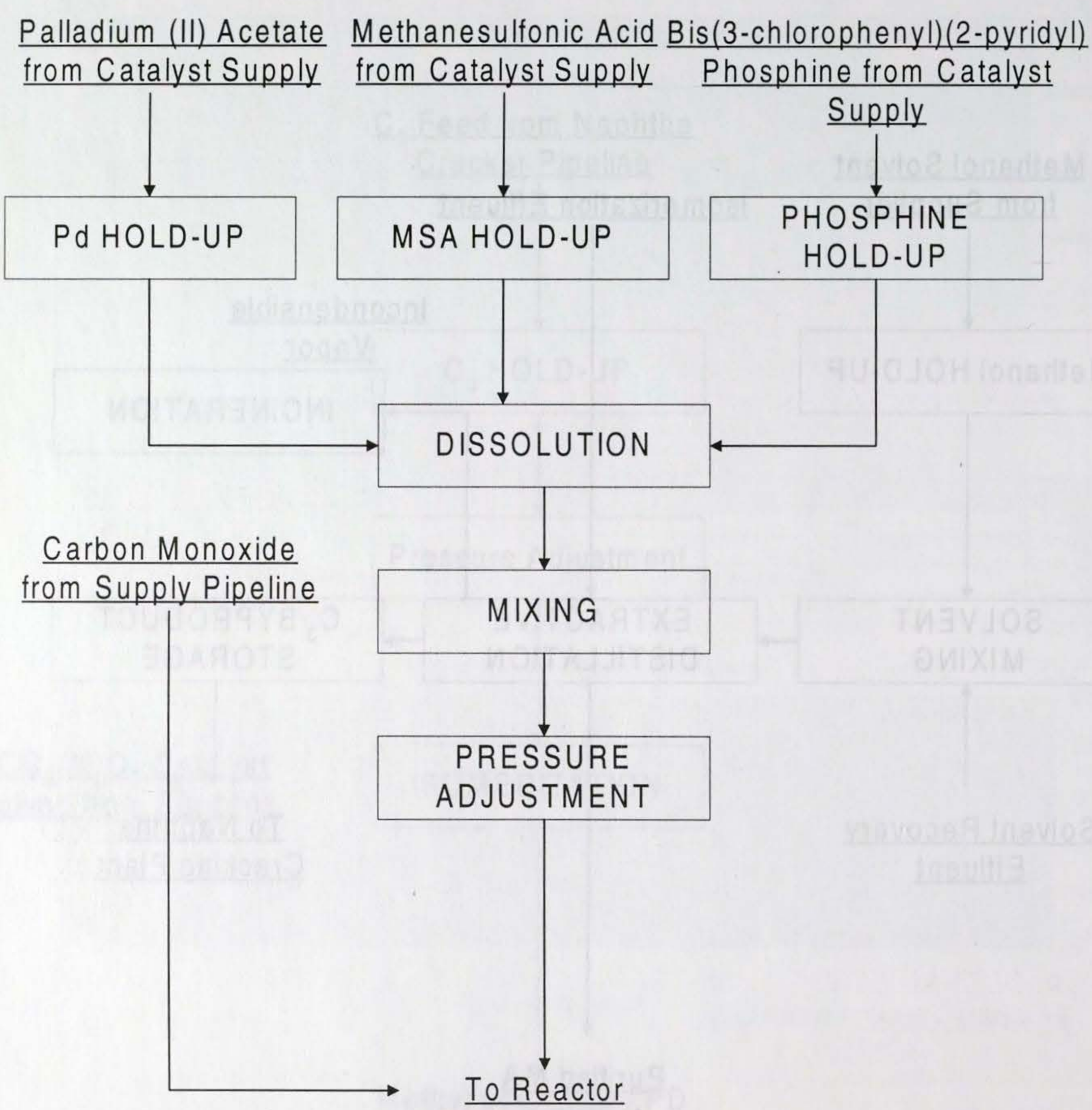
Section 100
Methyl acetylene/Propadiene Isomerization



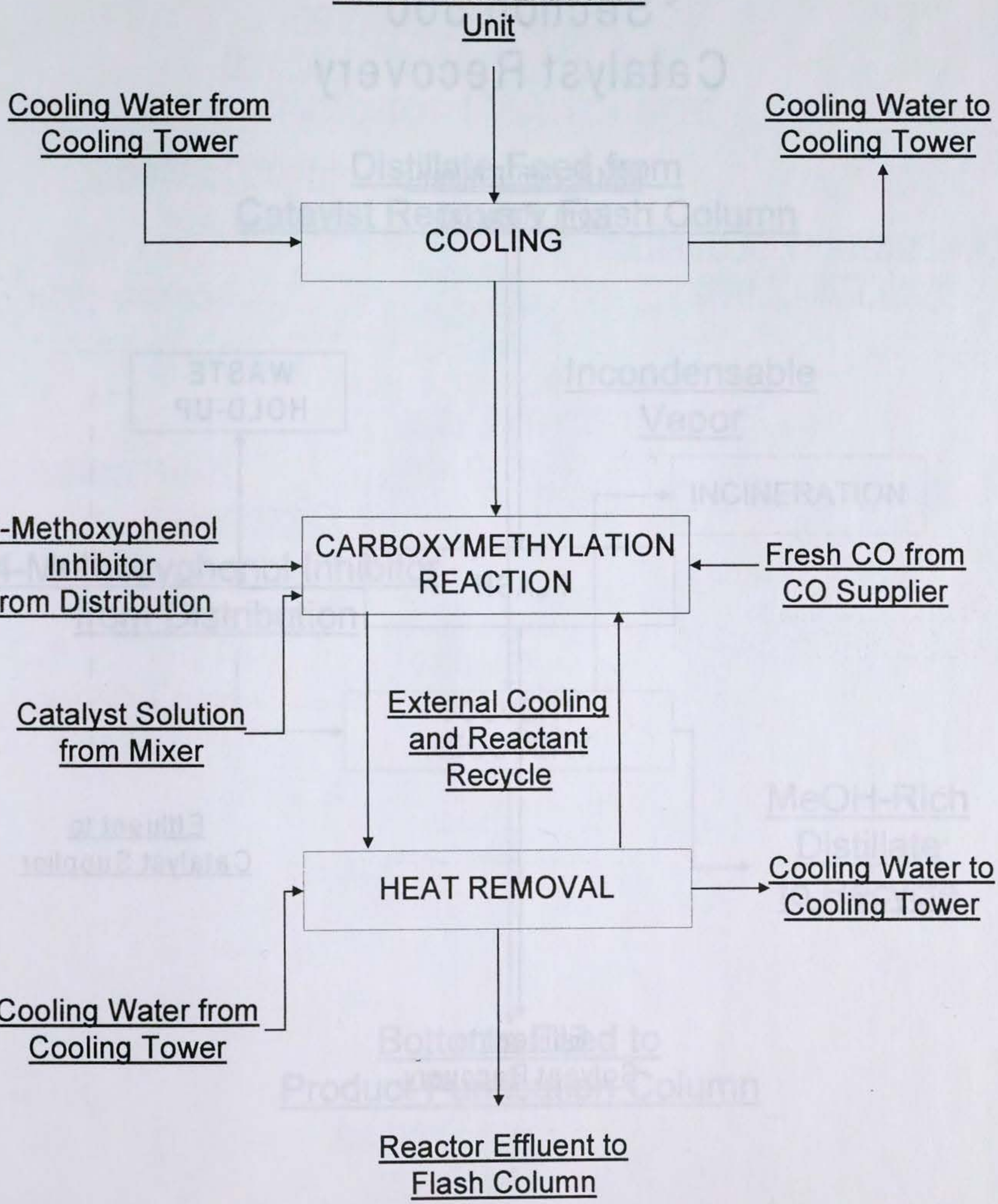
Section 200
Methyl acetylene Purification



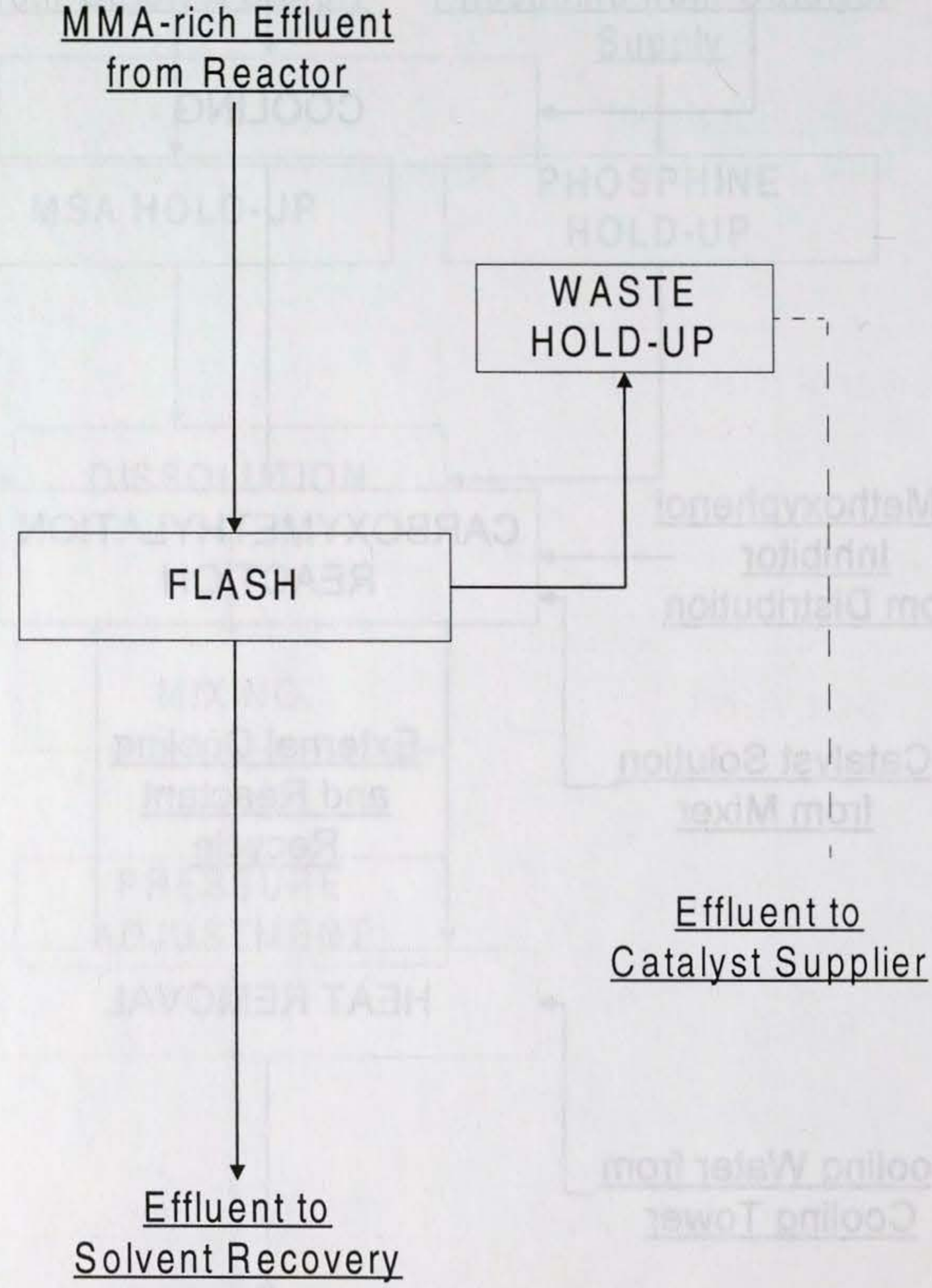
Section 300
Catalyst Preparation



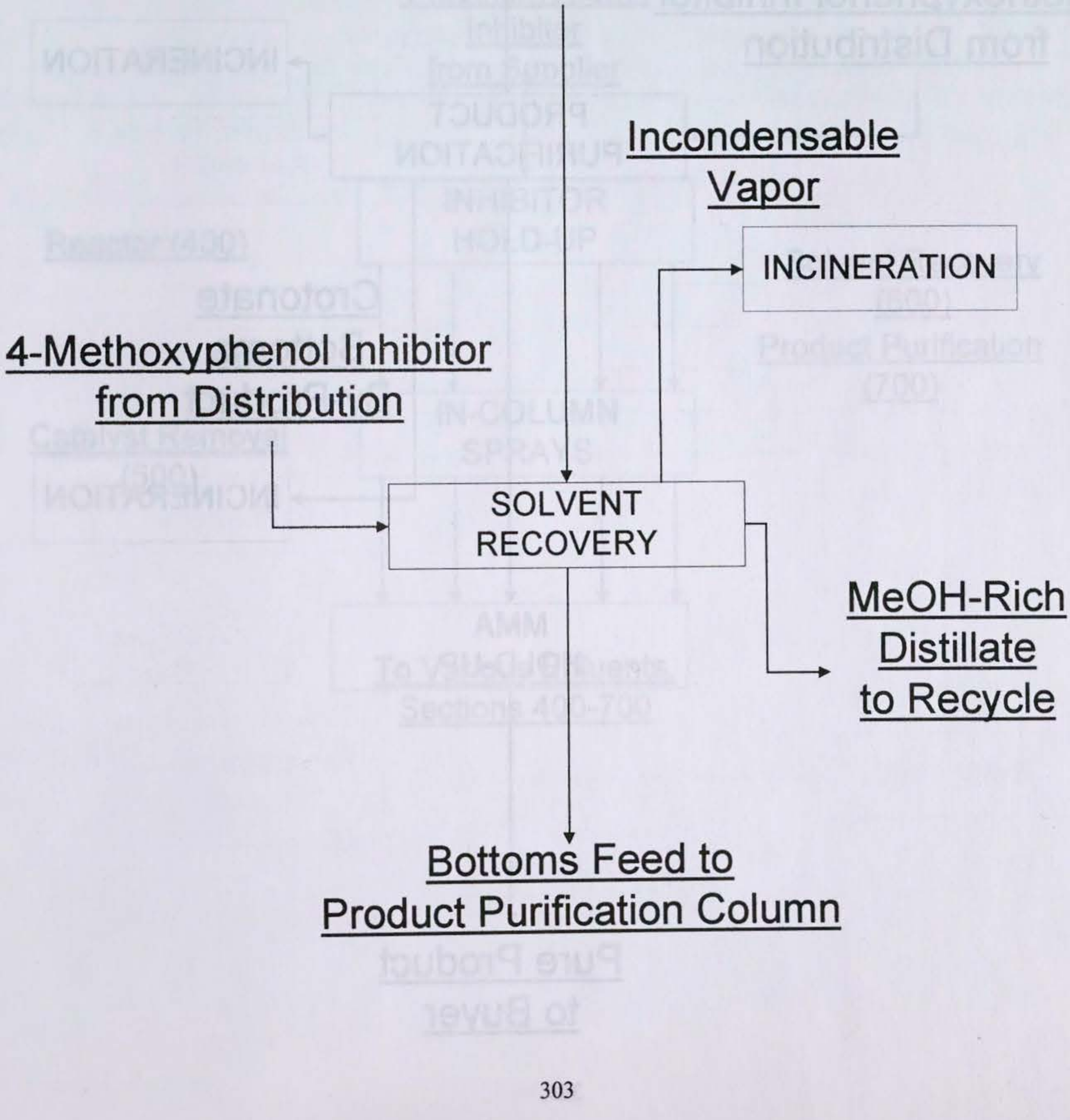
Section 400
Carboxymethylation Reaction



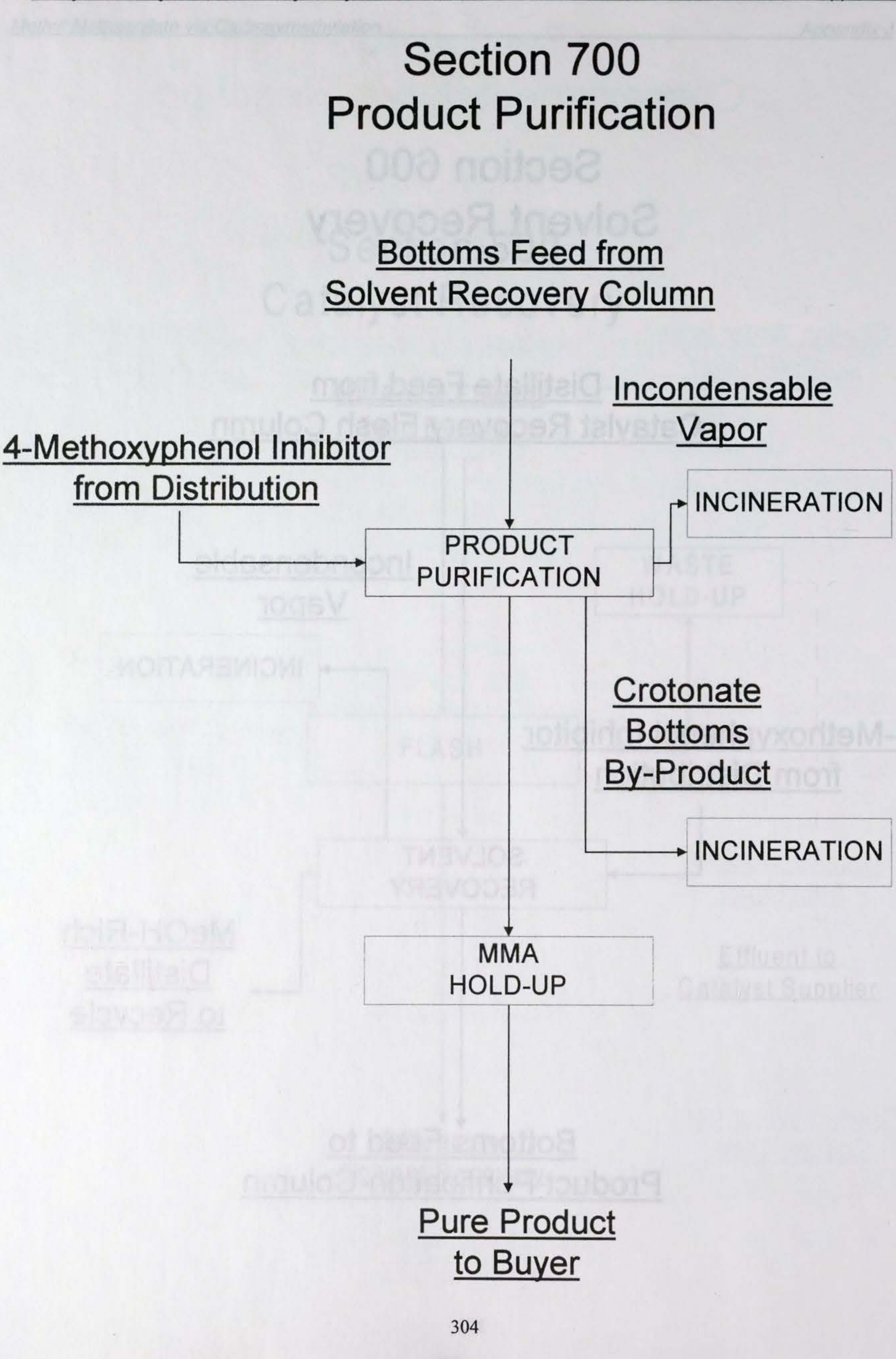
Section 500
Catalyst Recovery



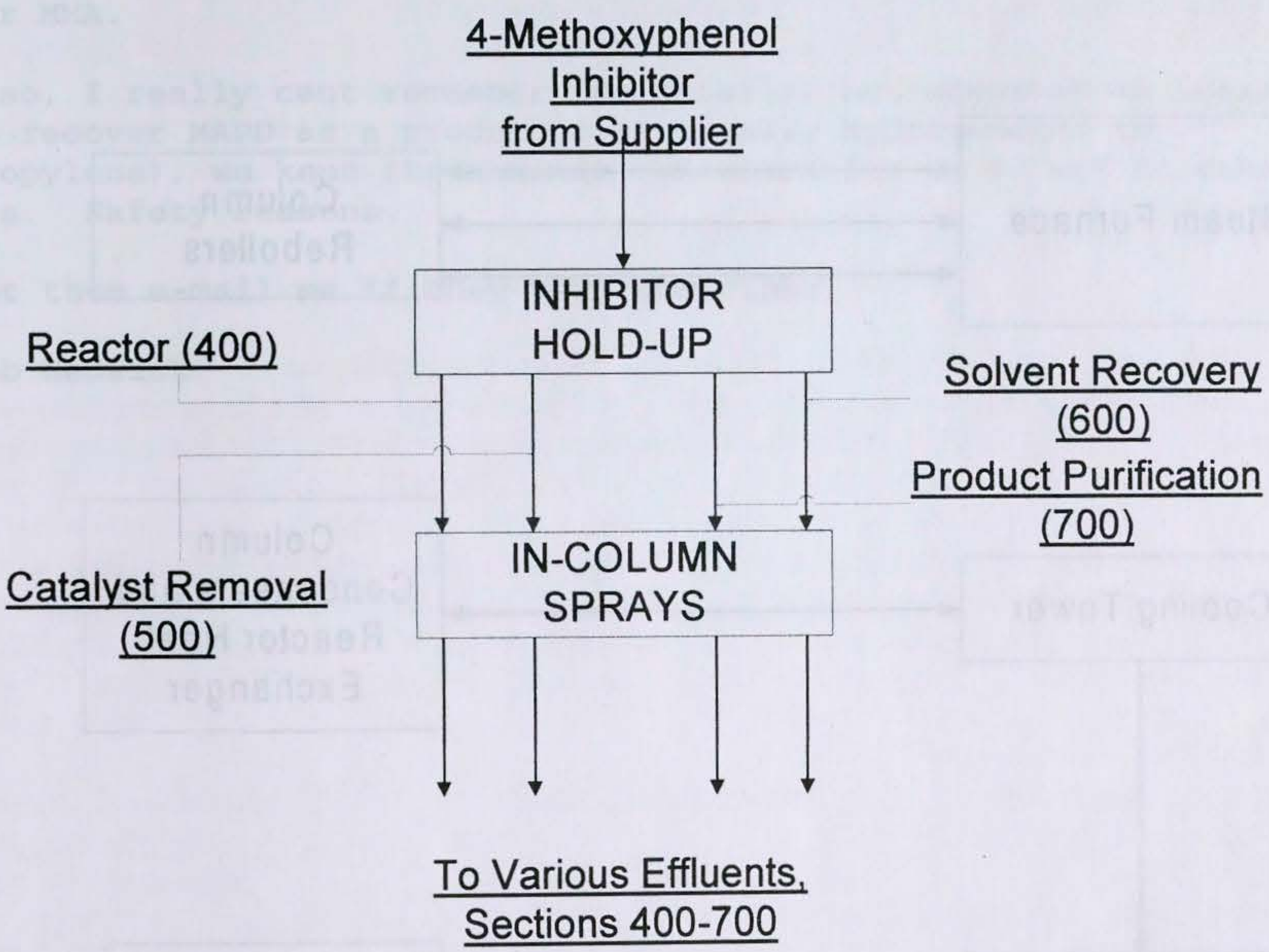
Section 600
Solvent Recovery



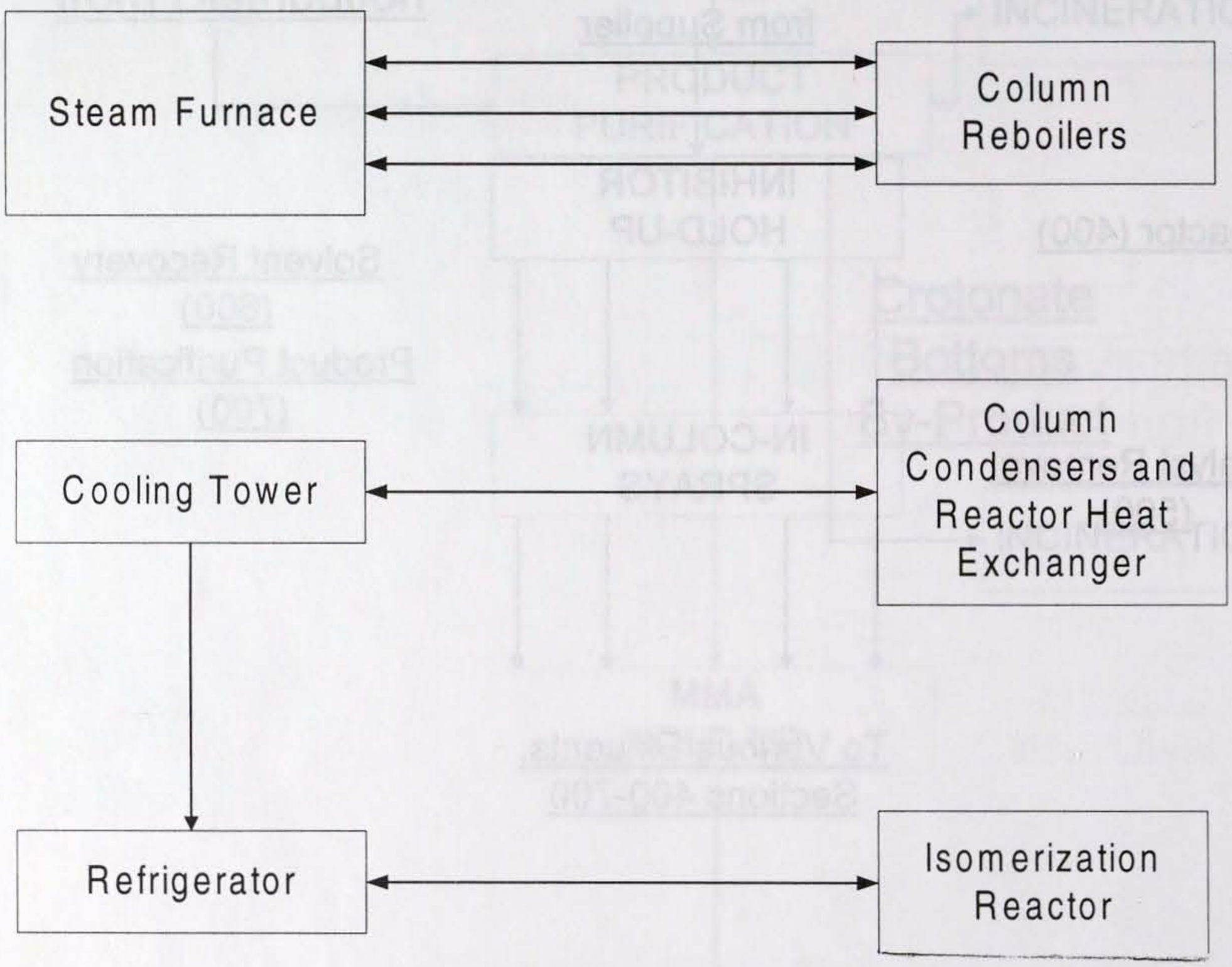
Section 700
Product Purification



Section 800
Inhibitor Distribution



Section 900
Utility Distribution Summary



K. Price Quotes from Industry Dealers

From: "Bob Nedwick" <CNSRXN@arcochem.com>
Date: Wed, 27 Jan 1999 17:09:48 -0500

The Propyne to MMA Team asked about the amount of Propyne produced in Olefins Plants. It appears that the yield from a naphtha feed plant is nominally 1.0 wt% of Methyl Acetylene (MA) plus Propadiene (PD) for maximum ethylene production mode (about 30% ethylene yield). Therefore, in a world size plant of 1500 MMlb/yr Ethylene, the MAPD will be about 1/30 th of the ethylene or 50 MMlb/yr. Of the total MAPD produced, about half is MA and half is PD, so one world scale plant produces 25 MMlb/yr propyne for MMA.

Also, I really cant remember the details, but whenever we looked to recover MAPD as a product (its usually hydrogenated to propylene), we kept its maximum concentration to 50 wt% in other C3s. Safety reasons.

Let them e-mail me if they have questions.

Bob Nedwick

Date: Mon, 08 Feb 1999 07:24:17 -0800
To: "Tofoomeister" <abmccabe@seas.upenn.edu>
From: Raymond Gorte <gorte@seas.upenn.edu>
Subject: Re: palladium diacetate catalyst

Adam,
I am willing to meet with your group, but believe that you should just go with the process as it has been given to you. While the idea of using solid or supported acids has gotten a lot of research attention, the idea has not been placed into practice on a large scale. If the substitution can be accomplished, it would require completely different operating conditions (i.e. a whole new design.).

Kudos to you for taking this initiative; however, unless you are able to find specific patents or something which describes the new process based on supported acids, I would not spend my time on this.

RJG

After meeting with Dr. Seider about our propyne to MMA plant design, he suggested we (Chris Brinkerhoff, Nitin Natesan, and Adam McCabe) meet with you to discuss a particular portion of our design.

Our reactor, which converts high-purity methyl acetylene to methyl methacrylate via a carboxymethylation reaction, requires the following three-part catalyst as suggested in the process patent:

- *palladium diacetate*
- *bis(3-chlorophenyl)(2-pyridyl)phosphine*
- *methanesulfonic acid*

This catalyst is described in the patent as a solution. However, the inclusion of a small amount of liquid catalyst that must be recovered presents significant design problems. The possibility of using a solid catalyst is much more attractive, but we are not sure of the feasibility of using a solid.

We were hoping that one (or both) of you could give us further information regarding the actual mechanism of a catalyst of this sort, so that we could determine how the catalyst is to be utilized in our design.

Date: Thu, 25 Mar 1999 15:55:40 +0000
From: "Connie Schlegel" <Schlece@Matthey.com>
Subject: palladium acetate catalyst -Reply

We do supply one of the three compounds that you are looking for, palladium acetate.

Due to the fact that part of the price component is the cost of the palladium metal, the unit price per gram of catalyst can fluctuate greatly based on the current market value of palladium. Based on today's market conditions, an approximate cost would b
e $7.50 per gram.

If I can be of further assistance, please let me know.

Regards,
Connie Schlegel

Dear Sir or Madam:

We are a chemical engineering design team at the University of Pennsylvania. We are currently researching the bulk price of a chemical in our catalyst, bis(3-chlorophenyl)(2-pyridyl)phosphine. We were unable to locate this chemical on your website, or in any other reference available to us. Our process requires approximately 500 kg/year of this phosphine to operate. Do you sell this chemical? If so, what would your bulk price be? If not, can you suggest another company that would sell or have price data for this chemical? Thank you for your time.

Chris Brinkerhoff
Adam McCabe
Nitin Natesan

please reply to: abmccabe@seas.upenn.edu

From: soneil@sial.com
Subject: Re: price/availability of a selected phosphine (fwd)
Date: Mon, 29 Mar 1999 14:15:22 -0500 (EST)

Dear Chris,
Thank you for your email. We do not offer this chemical, I suggest you check in a buyer's guide called Chem Sources or check out www.chemicalonline.com or any other buyer's guide to see if anyone is listing this chemical as one they have. You can also run a literature search in Chem Abstracts and see what information may be published regarding this chemical.
Thank you for your interest in Aldrich Chemical.
Sincerely,
Sarah O'Neil
Chemist, Technical Service

Dear Sir or Madam:

We are a chemical engineering design team at the University of Pennsylvania. We are currently researching the bulk price of a chemical in our catalyst, bis(3-chlorophenyl)(2-pyridyl)phosphine. We were unable to locate this chemical on your website, or in any other reference available to us. Our process requires approximately 500 kg/year of this phosphine to operate. Do you sell this chemical? If so, what would your bulk price be? If not, can you suggest another company that would sell or have price data for this chemical? Thank you for your time.

Chris Brinkerhoff
Adam McCabe
Nitin Natesan

please reply to: abmccabe@seas.upenn.edu

Subject: Attn; Nitin Natesan; Corrosive Acid Pump Application
To: nnatesan@seas.upenn.edu (Nitin Natesan)
Date: Tue, 30 Mar 1999 16:51:03 -0500 (EST)
From: barpump@ix.netcom.com

We recommend Wanner Hydra-Cell Pump Model F20BATJTTTMG Sealless Rotary Positive Displacement Hydraulically Actuated Balanced Single Acting Diaphragm Pump; "B" 0.28GPM CAM @1000PSI @1750RPM; Liquid End of Hastelloy "C" for Pump End, Valve Seat, Valve, Spring; Kynar Valve Spring Retainer; 1/2Inch Inlet X 3/8Inch Outlet NPTF Connections; Pump End Unitized to C236 Motor, 1/3 H.P., 1800 RPM, CS, TEFC, 1.15S.F., 1/60/115/208-230V., FLA 5.2/2.5-2.6; BHP 0.2409 for 1024cc/min @1000Psi; Accessory Required, BLACOH Model H 1180 V 4 Cu.In. Pulsation Dampener Rated to 1000Psi; Hastelloy C Liquid End with VITON Bladder; 3/8Inch Bottom NPTF Inlet Connection., **Net Price $1,819.00.,** Delivery Two Weeks., Ship Wt. 50 Lbs., Net Wt. 44 Lbs.

Regards, Robert W. Bergen, Barish Pump Co, Inc.
(barpump@ix.netcom.com)
P.S. Advise your fax number and we can send Lit. & Curve Cuts.

From: Christine Schmid <christine.schmid@merck.de>
Subject: Re: User's request to Merck-Schuchardt
Date: Wed, 14 Apr 1999 09:39:56 -0400 (EDT)

Dear Mr.Brinkerhoff,

thank you very much for your inquiry. We offer without engagement:
item 821233 4-Methoxyphenol >99%
20 x 25 kg DM 36,00/kg
delivery terms: net, incl.packing, fob German seaport
delivery time: shortly subject to prior sale

best regards
Dr.Th.Schuchardt (Merck-Schuchardt
an Associate of Merck KGaA,
Darmstadt/Germany)
C.Schmid

We are a senior design team at the University of Pennsylvania. We are currently designing a process that converts methyl acetylene to methyl methacrylate via carboxymethylation. Our process requires 1000 lb/yr of 4-methoxyphenol to inhibit MMA polymerization.

Can you provide us with a price quote for this amount of inhibitor?

Any information you have is greatly appreciated.

Chris Brinkerhoff
Adam McCabe
Nitin Natesan

please reply to: abmccabe@seas.upenn.edu

PFA Teflon Coated Thermowells

Model Number: B10 – B10 Series **$40**

- **Corrosion Resistant**
- **Nominal 0.020" Coating**
- **Available for all Thermowell Styles Except Flanged (1" Flange Only)**
- **Coating Rated to 400°F**
- **Available for Wells to 48" Long**

CLICK FOR LARGER IMAGE

Applications

- **Food & Beverage**
- **Pharmaceuticals**
- **Acids & Caustics**
- **Electroplating**
- **Corrosives**

Pricing for PFA coated wells is based on the overall length of the thermowell; the overall length of the thermowell; the overall length is equal to the insertion length plus hex, or socket length plus lag length. The total price is the price of the base thermowell plus the coating price.

Coating Pricing:	
To 12"	$40
To 18"	50
To 24"	60
Over 24"	Consult Quotations

Solid PFA Teflon Thermowells

WARNING! Because of Material Characteristics, These OMEGA Teflon Thermowells are for Static Fluid and Very Low Pressure Applications Only!

- **All Styles Except Flanged**
- **0.260" and 0.385" Bore Sizes**
- **Rated to 400°F at 15 PSIA**
- **Lengths to 10" Max**
- **Stainless Steel Insert for Added Strength**

Low Cost $^{1}/_{16}$ DIN LCD Temperature Controller and Industrial Timer

Model Number: PTC1A – PTC1A Series **$119**

- **Common Features**
- **Compact $^{1}/_{16}$ DIN Size**
- **Easy 2 Button Set-Up**
- **Clear LCD Display**
- **Panel or Socket Mount Design**

CLICK FOR LARGER IMAGE

Model PTC-1A

- **Internal Battery for Bench Set-Up**
- **Universal Power Supply 18 to 264 Vac/dc**
- **6 Programmable Time Ranges up to 99.9 Hrs**
- **6 Operating Modes**
- **Independent ON/OFF Cycling Mode**
- **Programmable without power supplied**

Model CN1A Series

- **Dual Outputs**
- **Thermocouple or RTD Input**
- **10 programmable alarm options**
- **Reverse (heat) or direct (Cool) control**
- **110 Vac, 240 Vac and 24Vac/Vdc Option**

The CN1A Temperature Controllers and PTC-1A Timer are low power, LCD control products designed to combine a harmonized appearance with simple to operate, flexible functions and high reliability. They are ideal for frequent user adjustable applications such as hot foil printing, window sealing, environmental ovens, which often require both temperature and timing control. The use of the PTC-SW Momentary Switch allows cycle reset from a remote location for the PTC-1A. Tamper proof range and mode settings for added security.

SPECIFICATIONS: Download complete Product Specifications in PDF format.

Common Specifications
Operating Ambient Range: 32 to 122°F (0 to 50°C)
Storage Temperature: -4 to 185°F (-20 to 85°C)
Dimensions: 1.9" H x 1.9" W x 3.5" D (48 x 48 x 89 mm)
Panel Cutout: 1.772" square (45 mm); $^{1}/_{16}$ DIN

Model CN1A Series
Programmable Functions: °C/°F, Hysteresis, Sensor type, Control action, Alarm conditions, setpoint limits, offset, password
Power: 120 Vac or 130 Vac, 47 to 63 Hz @ 1.5 VA max. Accuracy:
T/C: ±0.25% over 90% of scale range (-50 to 950°C) and ±1% over the extreme 5% of the scale limits (-99 to -51 and 950 to 999°C)
RTD: ±0.60% of full scale
Offset Accuracy: T/C: ±5°C; Pt100: ±2°C
Control Output: SPDT relay, rated @ 3A, 240 Vac
Alarm Output: SPST N.O. relay, rated @ 0.5A, 120 Vac
Sensor Options:

Pt100	-99 to 400°C (-99 to 700°F)
J	-99 to 700°C (-99 to 999°F)
K	-99 to 999°C (-99 to 999°F)
T	-99 to 300°C (-99 to 570°F)
N	-99 to 999°C (-99 to 999°F)

Model PTC-1A
Power: 18 to 264 Vac, 47 to 440 Hz, 18 to 300 Vdc
Power Consumption: 1 Watt
Scale Accuracy: ±20msec or ±0.5% of set time whichever is greater
Repeat Accuracy: ±0.3% of set time
Reset Time: 10 msec max.
Output: SPDT relay, rated 7A at 30 Vdc/240 Vac resistive
Electrical Life: 200,000 operations at rated load
Mechanical Life: 10 million operations
Isolation: 1500 Vac 50 Hz 1 minute

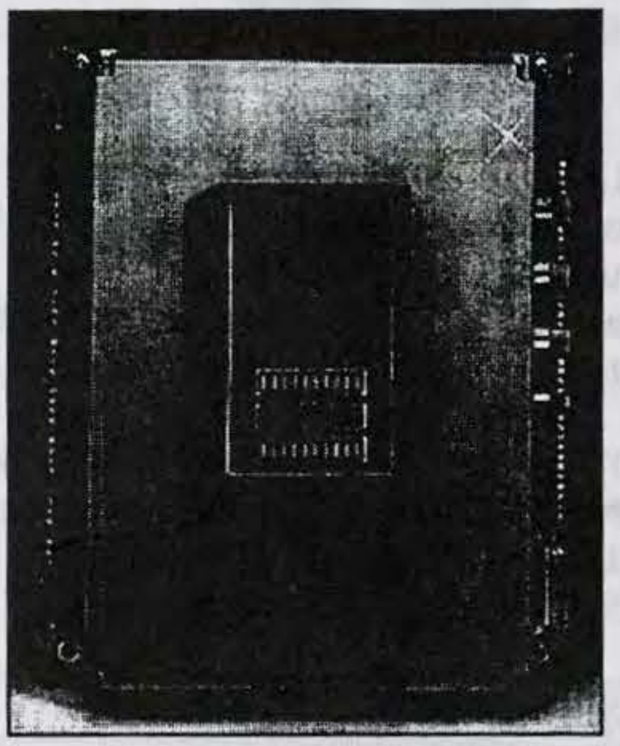
To Order *(Specify Model Number)*		
Model No.	**Price**	**Description**
PTC-1A	$119	Programmable Timer
CN1A-TC	139	J, K, T, N thermocouple input Controller, ON/OFF
CN1A-RTD	39	RTD input Controller, ON/OFF
PTC-SW	12	Momentary Reset Switch Accessory for PTC-1A

SALES OR SERVICE:
USA and CANADA: **1-888-663-4214**
OUTSIDE USA and CANADA: (USA) **203-359-1660**

Multi-Loop PID Temperature/Process Controller

Model Number: CN3390 **$2250**

- **10 PID Control Loops With Auto-Tuning**
- **J,K,T,E,R or S Thermocouple, RTD and 4-20 mA Current Input Types Selectable for Each Loop**
- **2 Alarm Setpoints per Loop**
- **Optical Isolation for Electrically Noisy Environments**
- **Relay, Triac, 4-20 mA and SSR Drive Plug-in Output Modules**
- **Optional RS-232, RS-422 and RS-485 Digital Communcations**
- **Coded Security Levels to Prevent Unauthorized Access to Programming**



Takes The Place of 10 Controllers

The OMEGA® CN3390 ON/OFF, proportional, PID Multi-Loop Temperature/Process Controller, measuring only 33/4" deep, features the inputs, outputs and programmable features and sophisticated control techniques typically found only in much larger controllers. The CN3390 requires only 30% of the mounting space required for 10 individual controllers. All hardwiring is done once on high quality plug-on terminal strips, so the unit can be easily installed or taken out of service.

The CN3390, with its optical isolation of inputs, outputs and the optional digital communications, is built to handle most real-world factory conditions without special filtering equipment, such as snubbers, isolated power supplies or noise suppressors.

Digital Signal Processing (DSP) sets the CN3390 controller apart from other multi-loop controllers. DSP maintains the integrity of the sensor input signals, resulting in more stable control. Over-sampling of inputs (92 times per second per input) and an input update rate of 0.5 seconds per loop, ensure that the CN3390 responds quickly to process changes.

Through simple programming selections you can adjust the controller displays to establish the range and engineering units of indication for the current input.

The CN3390 provides two alarm setpoints per loop (20) total, and an alarm LED for each loop. Any of these 20 setpoints may be connected to the common alarm output or one of ten optional alarm outputs. The common alarm output can be turned off from either the front panel alarm acknowledge pushbutton or from a remote pushbutton.

The CN3390 alarm setpoints may be mapped to an optional internal alarm board. The alarm boardês digital alarm outputs or the common alarm may be connected to a remote single

T110
C3 HOLDUP TANK

P110
C3 FEED PUMP

R150
ISOMERIZATION REACTOR

T210
METHANOL HOLDUP TANK

P210
METHANOL FEED PUMP

P230
METHANOL EXTRACTION FEED PUMP

D250 & 251
EXTRACTIVE DISTILLATION COLUMNS

P255
REFLUX PUMP

T255
REFLUX ACCUMULATOR

C260
CONDENSER

K270
REBOILER

P270
BOTTOMS PUMP

P280
DISTILLATE PUMP

T295
PROPANE HOLDUP TANK

T310
PdAC2 HOLDUP TANK

T320
BCPPP HOLDUP TANK

T330
MSA HOLDUP TANK

A350
CATALYST AGITATOR

M350
CATALYST MIXING TANK

P350
CATALYST BATCH FEED PUMP

P390
CATALYST REACTOR FEED PUMP

T395
CATALYST WASTE HOLDUP TANK

H410
PRE-REACTION HEAT EXCHANGER

H460
REACTOR HEAT EXCHANGER

R450
CSTR

A450
REACTOR AGITIATOR

S450
REACTOR INHIBITOR SPRAY

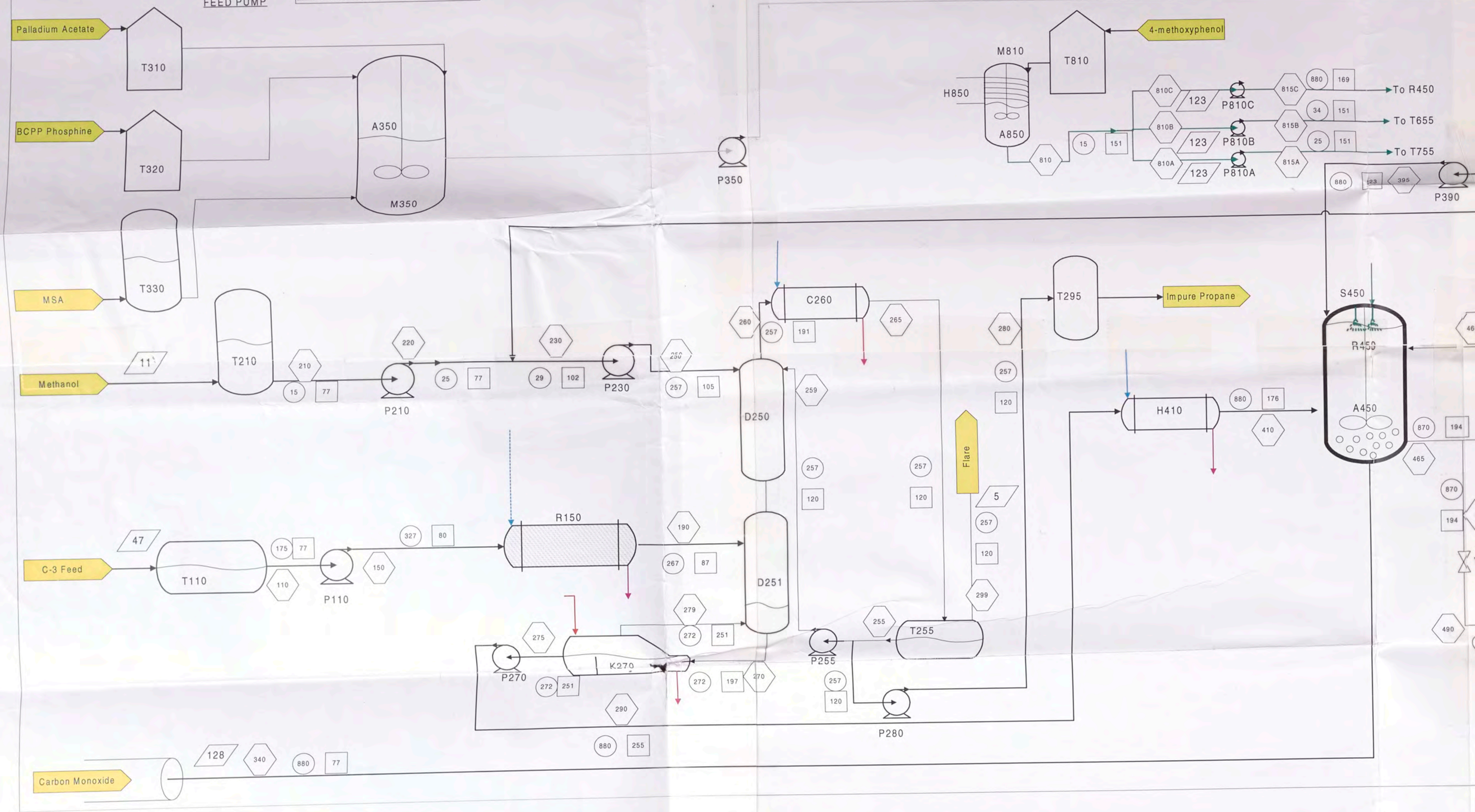
P450
REACTOR REFLUX PUMP

T550
FLASH COLUMN

B590
BLOWER/ COMPRESSOR

D6
AZEOT
DISTILL
COLU

T6
REF
ACCUMU



Stream ID		110	150	190	210	220	230	250	255	259	260	265	270	275	279	280	290	299	340	395	410	450	460	465	490	550	590	595	655	659	660	665	670	675	679	680	690
Temperature	°F	77.0	79.5	87.0	77.0	77.2	102	105	120	120	191	120	265	251	269	120	257	120	77.0	223	176	194	176	194	141	194	251	194	120	120	142	120	197	269	251	120	269
Pressure	psi	175	327	267	14.7	25.0	29.4	257	257	257	257	257	272	272	272	257	880	257	880	880	880	870	880	880	16.8	16.8	34.2	16.8	34.0	25.0	34.0	34.0	35.0	35.0	35.0	25.0	25.0
Vapor Frac		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	1.00	0.00	0.00	1.00	1.00	0.00	0.00	0.01	0.00	0.00	0.21	1.00	1.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00	1.00	0.00	0.00
Mass Flow	lb/hr	12,500	12,500	12,500	4,500	4,500	11,900	11,900	56,800	49,700	56,800	56,800	51,600	17,200	44,500	7,050	17,200	69.5	4,400	719	17,200	22,300	36,000	36,000	22,300	21,600	21,600	719	7,360	22,100	7,360	7,360	62,100	13,300	54,700	7,360	13,300
Volume Flow	gpm	46.5	46.7	46.5	11.3	11.3	28.7	28.8	246	216	246	246	176	55.7	145	30.6	56.1	4.92	128	1.61	50.1	57.0	92.1	92.1	3,330	16,700	8,900	1.57	17.5	52.5	17.5	17.5	152	32.8	135	17.5	32.8
Enthalpy	MMBTU/hr	3.28	3.31	3.17	-14.4	-14.4	-32.3	-32.2	-50.7	-44.4	-50.7	-50.7	-58.0	-20.1	-51.7	-6.31	-20.0	-0.06	-7.46	-1.34	-21.4	-42.5	-21.4	-21.4	-42.5	-36.9	-39.5	-1.35	-17.9	-53.6	-17.9	-17.9	-106	-21.4	-87.8	-17.9	-21.4
Mass Flow	lb/hr																	3.36	4,400	0.03	trace	673	1,090	1,090	673	673	673	0.03	9.9	29.7	9.9	9.9	9.9	trace	trace	9.9	trac
CO									501	439	501	501	62.3	trace	trace	62	trace	0.72			trace																
C_3H_6		63.0	63.0	63.0					51,400	45,000	51,400	51,400	6,400	1.76	4.56	6,390	1.76	61.0		<0.001	1.76	1.76	2.85	2.85	1.76	1.76	1.76	<0.001	0.93	2.78	0.93	0.93	0.93	trace	trace	0.93	trac
C_3H_8		6,450	6,460	6,450			0.93	0.93	4,360	3,810	4,360	4,360	808	103	267	541	103	4.33		0.12	103	103	167	167	103	103	103	0.12	56.1	168	56.1	56.1	56.1	trace	trace	56.1	trac
PD		2,970	2,970	592			56.1	56.1	<0.001	<0.001	<0.001	<0.001	13,800	5,330	13,800	<0.001	5,330	trace			5,330															
MA		2,970	2,970	5,330					<0.001	<0.001	<0.001	<0.001	21,600	8,300	21,500	39.5	8,300	<0.001		21.1	8,300	4,060	6,560	6,560	4,060	4,040	4,040	21.1	3,840	11,600	3,840	3,840	3,860	4.23	17.4	3,840	4.2
MEOH					4,500	4,500	8,340	8,340	317	278	317	317	8,910	3,440	8,900	5.11	3,440	trace		602	3,440	17,200	27,800	27,800	17,200	16,600	16,600	602	3,440	10,400	3,440	3,440	57,400	13,100	53,900	3,440	13,10
MMA							3,440	3,440	41.1	36.0	41.1	41.1	42.7	16.5	42.7	<0.001	16.5	trace		15.8	16.5	232	375	375	232	216	216	15.8	16.5	49.6	16.5	16.5	837	200	820	16.5	20
MC							16.5	16.5	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	trace	<0.001	trace		71.6	<0.001	71.6	116	116	71.6	0.10	0.10	71.5	<0.001	<0.001	<0.001	<0.001	0.40	0.10	0.39	<0.001	0.1
MSA							<0.001	<0.001	trace	trace	trace	trace																									
H_2O																	0.1	trace		6.70	0.12	7.20	11.6	11.6	7.20	0.37	0.37	6.70	0.12	0.37	0.12	0.12	3.70	0.87	3.57	0.12	0.8
MOP							0.12	0.12	trace	trace	trace	trace	0.32	0.12	0.32	trace	trace	trace		2.08	trace	2.08	3.35	3.35	2.08	trace	trace	2.07	trace	trace	trace	trace	trace	trace	trace	trace	trac
PA							trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace		246	<0.001	246	397	397	246	<0.001	<0.001	246	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.00
BCPPP							<0.001	<0.001	trace	trace	trace	trace	<0.001	<0.001	<0.001	trace	<0.001	trace																			

Note: Streams 310, 320, 330, 350, 355, 595, and 805 are batch process streams and are therefore not included in this table.

T550 FLASH COLUMN

B590 BLOWER/ COMPRESSOR

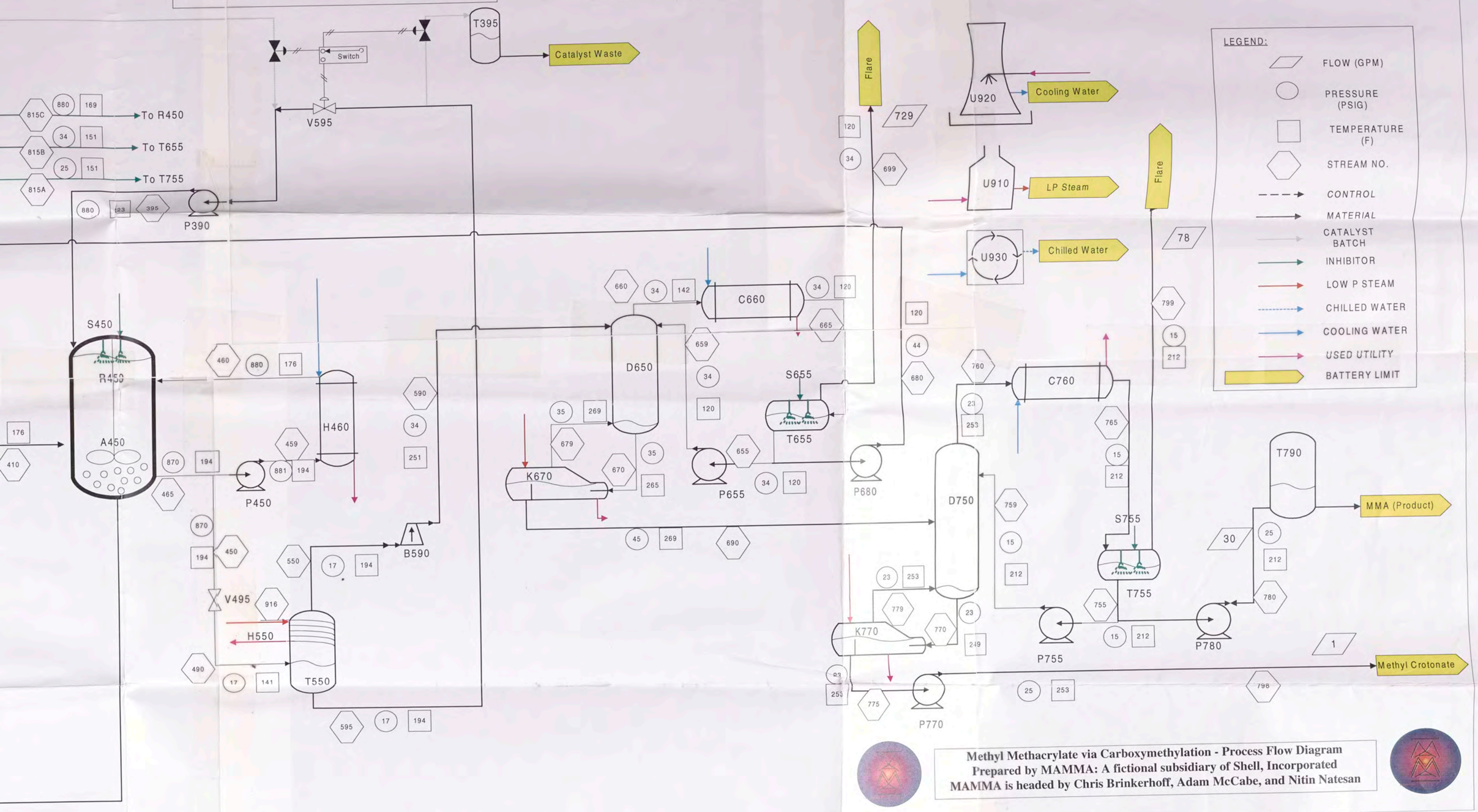
D650 AZEOTROPIC DISTILLATION COLUMN
T655 REFLUX ACCUMULATOR
S655 REFLUX INHIBITOR SPRAY
P655 REFLUX PUMP
C660 CONDENSER
K670 REBOILER
P680 DISTILLATE PUMP

D750 CROTONATE REMOVAL DISTILLATION COLUMN
T755 REFLUX ACCUMULATOR
S755 REFLUX INHIBITOR SPRAY
P755 REFLUX PUMP
C760 CONDENSER
K770 REBOILER
P770 BOTTOMS PUMP
P780 DISTILLATE PUMP

T790 PRODUCT HOLDUP TANK

T810 INHIBITOR HOLDUP TANK
M810 INHIBITOR MIXING TANK
A850 INHIBITOR AGITATOR
P810A, B, C INHIBITOR FEED PUMPS
H850 INHIBITOR HEATER

U910 STEAM FURNACE
U920 COOLING TOWER
U930 REFRIGERATOR



Methyl Methacrylate via Carboxymethylation - Process Flow Diagram
Prepared by MAMMA: A fictional subsidiary of Shell, Incorporated
MAMMA is headed by Chris Brinkerhoff, Adam McCabe, and Nitin Natesan

	665	670	675	679	680	690	699	755	759	760	765	770	775	779	780	798	799	810	810A	810B	810C	815A	815B	815C	910	912	914	921	922	923	924	925	930	970	972	974	981	982	983	984	985	990
Temperature (F)	120	197	269	251	120	269	120	212	212	212	212	249	253	253	212	253	212	151	151	151	151	151	151	169	371	371	371	90.0	90.0	90.0	90.0	90.0	45.0	212	212	212	120	121	120	120	120	67.0
Pressure (PSIG)	34.0	35.0	35.0	35.0	25.0	25.0	34.0	14.7	25.0	14.7	14.7	23.4	23.4	23.4	25.0	25.0	14.7	14.7	14.7	14.7	14.7	25.0	34.0	880	175	175	175	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7
Vapor Fraction	0.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00	0.00	1.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	1.00	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mass Flow (lb/hr)	360	62,100	13,300	54,700	7,360	13,300	1,010	12,700	59,500	12,700	12,700	83,600	463	70,900	12,700	463	127	1.60	0.77	0.56	0.27	0.77	0.56	0.27	9,510	10,400	7,200	263,000	49,800	418,000	690,000	316,000	6,230	9,510	10,400	7,200	263,000	49,800	418,000	690,000	316,000	6,230
Volume (ft3/hr)	7.5	152	32.8	135	17.5	32.8	729	29.8	139	29.8	29.8	204	1.14	175	29.8	1.14	77.9	0.0029	0.0014	0.0010	0.0005	0.0014	0.0010	0.0005	3,090	3,380	2,340	526	101	836	1,380	631	12.0	19.0	20.8	14.4	526	103	836	1,380	631	12.0
Heat Flow (MMBtu/hr)	7.9	-106	-21.4	-87.8	-17.9	-21.4	-1.70	-20.8	-97.5	-20.8	-20.8	-134	-0.74	-113	-20.8	-0.74	-0.19	-0.002	-0.001	-0.001	>-0.001	-0.001	-0.001	>-0.001	-11.4	-12.4	-8.61	-1790	-339	-2850	-4700	-2160	-42.4	-1.71	-1.87	-1.30	-1790	-337	-2840	-4680	-2150	-42.2
Component Flow (lb/hr)																																										
Methyl Methacrylate	9.9	9.9	trace	trace	9.9	trace	663																																			
Methyl Crotonate																																										
Methanol	0.93	0.93	trace	trace	0.93	trace	0.84	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace																										
Water	56.1	56.1	trace	trace	56.1	trace	47.2	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace																										
Methacrylic Acid																																										
Crotonic Acid	840	3,860	4.23	17.4	3,840	4.23	193	3.84	18.0	3.84	3.84	3.84	trace	trace	3.84	trace	0.38																										
Methyl Methacrylate	440	57,400	13,100	53,900	3,440	13,100	105	12,700	59,500	12,700	12,700	52,800	262	40,100	12,700	262	126																										
Methyl Crotonate	16.5	837	200	820	16.5	200	0.10	trace	trace	trace	trace	30,600	200	30,600	trace	200	trace																										
Inhibitor	001	0.40	0.10	0.39	<0.001	0.10	trace	trace	trace	trace	trace	14.7	0.10	14.7	trace	0.10	trace																										
Water																									9,510	10,400	7,200	263,000	49,900	418,000	690,000	316,000	6,230	9,510	10,400	7,200	263,000	49,900	418,000	690,000	316,000	6,230
Methacrylic Acid	0.12	3.70	0.87	3.57	0.12	0.87	trace	0.12	0.58	0.12	0.12	228	1.49	228	0.12	1.49	trace	1.61	0.74	0.62	0.25	0.74	0.62	0.25																	
Crotonic Acid	race	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace	trace																										
Methanol	001	<0.001	<0.001	<0.001	<0.001	<0.001	trace	trace	trace	trace	trace	<0.001	<0.001	<0.001	trace	<0.001	trace																										